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Experiments relating to phthiocerol. Part II. Synthesis of (+)-6-methoxy-6-methylnonanoic acid. By J. W. Lewis and N. Polgar

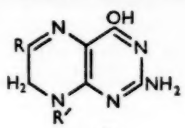
835. *Pteridine Derivatives. Part V.* The Synthesis of 2 : 8-Dihydro-2-imino-8-alkylpteridines.*

By W. E. Fidler and H. C. S. Wood.

Condensation of several 2 : 5-diamino-4-alkyl(and aryl)aminopyrimidines with 1 : 2-diketones to give 2 : 8-dihydro-2-imino-8-alkyl(and aryl)pteridines is described. The structures assigned to a pteridine isolated from the eyes of *Drosophila melanogaster*, and to luciferesceine, are discussed in the light of the properties of these synthetic compounds.

Forrest and Mitchell [1] recently reported the isolation of a pteridine from the eyes of the fruit fly, *Drosophila melanogaster*. They assigned structure (I; R = CO_2H, R′ = CO·CHMe·OH) to this compound. A modified structure (II; R = CO_2H, R′ = CO·CHMe·OH) has been suggested [2] by one of us which helps to explain the similarity of the ultraviolet absorption spectrum of this pigment to that of riboflavin.

The evidence for these structures, however, is not conclusive. Forrest and Mitchell report the formation of an oxime and a 2 : 4-dinitrophenylhydrazone from the pigment, and they consider the carbonyl group which gives rise to these derivatives to be that attached at position 8. This carbonyl function is, however, part of an amide group and is not likely to form normal carbonyl derivatives.



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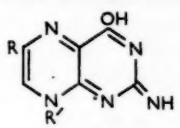

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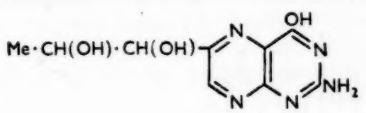

(III)

Alkaline hydrolysis of either the oxime or the dinitrophenylhydrazone of the pigment gave 2-amino-4-hydroxypteridine-6-carboxylic acid, and Forrest and Mitchell assume that the carboxyl group exists as such in the pigment. 6-Formylpteridines are known, however, to disproportionate in alkali to the acid and the more soluble hydroxymethyl compound.[3] The carboxyl group in the hydrolysis product could thus be formed from either a formyl group or a lactoyl group at position 6 in the original substance. This suggests one or other of the alternative structures (I; R = CHO, R′ = CO·CHMe·OH, and *vice versa*) for the pigment. We prefer the latter structure on grounds of biogenetic theory because of the similarity to a second pteridine which has been isolated from *Drosophila* and identified [4] as 2-amino-4-hydroxy-6-(1 : 2-dihydroxypropyl)pteridine (III). The ultraviolet absorption spectrum [1] of the pigment differs from that of known 7 : 8-dihydropteridines [5] and from that of 2-amino-7 : 8-dihydro-4-hydroxy-8-methyl-6 : 7-diphenylpteridine, prepared by condensation of benzoin with 2 : 5-diamino-4-hydroxy-6-methylaminopyrimidine. We suggest that a structure (II; R = CO·CHMe·OH, R′ = CHO or more probably CH_2·OH), which has a *para*-quinonoid type of structure similar to that found in riboflavin, is in better agreement with the published data, and we retract our previous structure (II; R = CO_2H, R′ = CO·CHMe·OH).

We now report the synthesis of 2 : 8-dihydro-4-hydroxy-2-imino-6 : 7 : 8-trimethylpteridine (IV; R = R′ = Me, R″ = H) which has a chromophoric system similar to that

* Part IV, *J.*, 1957, 3980.

[1] Forrest and Mitchell, *J. Amer. Chem. Soc.*, 1954, **76**, 5658.

[2] Wood, Ciba Symposium on the "Chemistry and Biology of Pteridines," Churchill, London, 1954, p. 154.

[3] Waller, Goldman, Angier, Boothe, Hutchings, Mowat, and Semb, *J. Amer. Chem. Soc.*, 1950, **72**, 4630.

[4] Forrest and Mitchell, *ibid.*, 1955, **77**, 4865.

[5] Boothe *et al.*, *ibid.*, 1948, **70**, 27.

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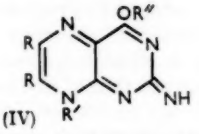
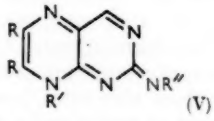
proposed above for the *Drosophila* pigment. 2-Amino-4-chloro-6-hydroxypyrimidine with methylamine at 120° gave 2-amino-4-hydroxy-6-methylaminopyrimidine. The derived 5-nitrosopyrimidine was reduced with sodium dithionite to 2 : 5-diamino-4-hydroxy-6-methylaminopyrimidine. Condensation with diacetyl gave 2 : 8-dihydro-4-hydroxy-2-imino-6 : 7 : 8-trimethylpteridine (IV; R = R′ = Me, R″ = H), the ultraviolet absorption spectrum of which bears no formal resemblance to that of the *Drosophila* pigment but has similar long-wavelength absorption (395 mμ at pH 1). Since few pteridines (the exceptions being mercaptopteridines) exhibit such absorption, some similarity in structure between the two compounds is indicated. The 6 : 7-diphenyl analogue (IV; R = Ph, R′ = Me, R″ = H) was synthesised by condensation of 2 : 5-diamino-4-hydroxy-6-methylaminopyrimidine with benzil.

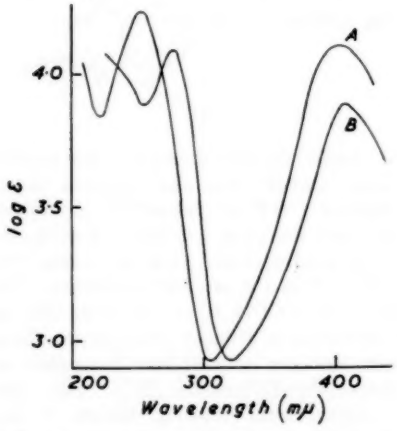


(IV)



(V)

The synthesis of 4-ethoxy-2 : 8-dihydro-2-imino-6 : 7 : 8-trimethylpteridine (IV; R = R′ = Me, R″ = Et) was also undertaken. Treatment of 2-amino-4-chloro-6-methylaminopyrimidine with sodium ethoxide in dry ethanol gave 2-amino-4-ethoxy-6-methylaminopyrimidine. The ethoxy-compound was coupled with *p*-chlorobenzenediazonium



Absorption spectra in 0·1N-*hydrochloric acid of* (*A*) 4-*ethoxy*-2 : 8-*dihydro*-2-*imino*-6 : 7 : 8-*trimethylpteridine and* (*B*) Drosophila *pigment*.[1]

chloride and then reduced, to give the unstable 2 : 5-diamino-4-ethoxy-6-methylaminopyrimidine. This was condensed directly with diacetyl to give the iminopteridine (IV; R = R′ = Me, R″ = Et). The last compound shows ultraviolet absorption at much longer wavelength in acid solution than does the 4-hydroxy-analogue (IV; R = R′ = Me, R″ = H), and we attribute this to the true *para*-quinonoid structure of the ethoxy-compound: the 4-hydroxy-compound in acid solution probably exists in the cyclic amide form [6] with consequent reduction of the chromophoric system. The spectrum of the ethoxyiminopteridine (IV; R = R′ = Me, R″ = Et) is so similar to that [1] of the *Drosophila* pigment (see Figure) that we consider that the latter must also have this true *para*-quinonoid structure.

The conversion of the naturally occurring purines into 8-substituted pteridines, *via* the intermediate 4-alkylamino-5-aminopyrimidines, has been discussed by Albert.[7] As

[6] Cf. Part IV, *J.*, 1957, 3980.
[7] Brown and Mason, *J.*, 1956, 3443.

the naturally occurring pteridines invariably have a 2-amino-group we now describe the condensation of several 2 : 5-diamino-4-alkyl(and aryl)aminopyrimidines with 1 : 2-diketones to give pteridines of structure (V).

2 : 8-Dihydro-2-imino-6 : 7 : 8-trimethylpteridine (V; R = R′ = Me, R″ = H) was synthesised by condensation of diacetyl with 2 : 5-diamino-4-methylaminopyrimidine. The latter was prepared from the known 2-amino-4-chloro-6-methylaminopyrimidine which was dechlorinated to give 2-amino-4-methylaminopyrimidine. Condensation with *p*-chlorobenzenediazonium chloride followed by catalytic hydrogenation gave the required pyrimidine. The ultraviolet absorption spectrum of the neutral molecule of the 2-iminopteridine (V; R = R′ = Me, R″ = H) closely resembles those of the 8-alkyl-2-pteridones (Part IV [6] and Table). Unlike the pteridones the imino-compound has no tendency to hydration in the solid state. The pK_a value (5·60) is higher than any previously recorded for a simple aminopteridine; the corresponding value for 2-aminopteridine is 4·2. This agrees with Angyal and Angyal's observation [8] that amino-groups kept in the imino-form by alkylation of a ring nitrogen atom have a high pK_a value.

The 2-iminopteridine gave a monoacetyl derivative which absorbs at a longer wavelength in the ultraviolet region than the parent iminopteridine. This is contrary to previous observations on the spectra of acetylated aminopteridines where acetylation decreases the wavelength of maximum absorption.[9] The anomaly is due to the increase in conjugation provided by the acetyl group of the acetyliminopteridine; no such increase in conjugation is conferred by the acetyl group in an acetamidopteridine.

A cream-coloured substance, luciferescein, has been isolated by Strehler [10] from the head of the firefly *Photinus pyralis*. Albert [11] suggests that it may be the iminoribitylpteridine (V; R = R″ = H, R′ = ribityl) and points out the analogy with riboflavin.

Absorption spectra (in water).

Substance	$\lambda_{max.}$ (mμ)	ε	pH
2 : 8-Dihydro-4-hydroxy-2-imino-6 : 7 : 8-trimethylpteridine	223; 268; 306; 365	18,500; 8,950; 11,000; 6,800	13
	254; 284; 395	12,100; 13,150; 12,500	1
2 : 8-Dihydro-4-hydroxy-2-imino-8-methyl-6 : 7-diphenylpteridine	218; 267; 380	39,000; 24,000; 13,700	13
2-Amino-7 : 8-dihydro-4-hydroxy-8-methyl-6 : 7-diphenylpteridine	260; 398	9,700; 6,700	13
4-Ethoxy-2 : 8-dihydro-2-imino-6 : 7 : 8-trimethylpteridine	<220; 255; 405	>10,000; 17,600; 13,000	1
	234; 301; 361 [a]	24,350; 14,100; 10,200	—
2 : 8-Dihydro-2-imino-6 : 7 : 8-trimethylpteridine	235; 328	20,400; 9,900	1
	238; 340	18,900; 12,200	7
2-Acetylimino-2 : 8-dihydro-6 : 7 : 8-trimethylpteridine	226; 250 [b]; 318; 364 [a]	25,500; 9,400; 7,150; 6,100	—
2 : 8-Dihydro-6 : 7 : 8-trimethyl-2-methyliminopteridine	248; 352 [a]	23,000; 17,350	—
2 : 8-Dihydro-6 : 7 : 8-triphenyl-2-phenyliminopteridine	<220; 360 [a]	>30,000; 23,200	—
2 : 8-Dihydro-6 : 7-dimethyl-8-phenyl-2-phenylimino-pteridine	245; 269; 370 [a]	15,700; 18,850; 16,150	—

[a] In EtOH. [b] Shoulder.

Comparison of the ultraviolet absorption spectrum of luciferescein with that of 2 : 8-dihydro-2-imino-6 : 7 : 8-trimethylpteridine (V; R = R′ = Me, R″ = H) shows no similarity. The pK_a (5·60) of (V; R = R′ = Me, R″ = H) is also much lower than that quoted for luciferescein. We thus consider the structure suggested by Albert is unlikely to be correct.

[8] Angyal and Angyal, *J.*, 1952, 1463.
[9] Albert, Brown, and Wood, *J.*, 1954, 3832.
[10] Strehler, *Arch. Biochem. Biophys.*, 1951, **32**, 397.
[11] Albert, "Fortschritte der Chemie Organischer Naturstoffe," Springer-Verlag, Vienna, 1954, p. 387.

A series of 2-alkylimino- and 2-arylimino-pteridines was synthesised by a common method. Reaction of 2 : 4-dichloro-5-nitropyrimidine with methylamine, aniline, and benzylamine gave the 2 : 4-dialkylamino(or diarylamino)-5-nitropyrimidine. Catalytic hydrogenation of these nitropyrimidines gave the 5-aminopyrimidines which were condensed directly with one or more of the dicarbonyl compounds, glyoxal, diacetyl, and benzil. The products were 2 : 8-dihydro-2-iminopteridines of general structure (V), which exhibit ultraviolet absorption characteristic of the *para*-quinonoid system of double bonds (Table and Part IV [6]). The pK_a value of the methyliminopteridine (VII; R = R′ = R″ = Me) is 6·1, in agreement with the observation [12] that methylation of an amino-group raises the pK_a value by about 0·3 unit.

Experimental

For general instructions see Part IV [6].

2-Amino-4-hydroxy-6-methylaminopyrimidine.—2-Amino-4-chloro-6-hydroxypyrimidine [13] (8·5 g.) and ethanolic methylamine (33% w/w; 25 c.c.) were heated in a sealed tube at 120° for 4 hr. The solution was cooled, and the precipitate was collected and dissolved in hot dilute hydrochloric acid (30 c.c.). The acid solution was treated with charcoal, and sodium hydrogen carbonate was added to give *2-amino-4-hydroxy-6-methylaminopyrimidine* (3·7 g.). Recrystallisation from ethanol gave light brown plates, m. p. 255—257° (Found: C, 43·1; H, 5·6; N, 39·6. $C_5H_9ON_4$ requires C, 42·9; H, 5·8; N, 40·0%).

2-Amino-4-hydroxy-6-methylamino-5-nitrosopyrimidine.—2-Amino-4-hydroxy-6-methylaminopyrimidine (2·5 g.) in 2N-hydrochloric acid (45 c.c.) was treated dropwise at 0° with sodium nitrite (2 g.) in water (25 c.c.). After being chilled overnight, the precipitate was collected, and recrystallised from water (160 parts) to give the *5-nitrosopyrimidine* (2·3 g.) as red needles, m. p. >300° (Found: C, 35·6; H, 4·1; N, 41·1. $C_5H_7O_2N_5$ requires C, 35·5; H, 4·2; N, 41·4%).

2 : 5-Diamino-4-hydroxy-6-methylaminopyrimidine.—2-Amino-4-hydroxy-6-methylamino-5-nitrosopyrimidine (0·5 g.) in hot sodium hydroxide solution (0·72 g. in 8 c.c. water) was heated to 80° on the water-bath, and a vigorous stream of nitrogen was bubbled through the solution. Sodium dithionite (2 g.) was added during 5 min., the colour of the solution changing from deep red to yellow. Heating under nitrogen was continued for a further 20 min., concentrated hydrochloric acid was added to pH 9·5, and the solution was chilled. The rather unstable *2 : 5-diamino-4-hydroxy-6-methylaminopyrimidine* (0·35 g.) was collected. The compound, m. p. 204—210° (decomp.), decomposed rapidly on attempted recrystallisation (Found: C, 38·0; H, 6·1. $C_5H_9ON_5$ requires C, 38·75; H, 5·8%).

2 : 8-Dihydro-4-hydroxy-2-imino-6 : 7 : 8-trimethylpteridine.—2 : 5-Diamino-4-hydroxy-6-methylaminopyrimidine (0·31 g.), acetic acid (3 c.c.), and water (20 c.c.) were warmed gently on the steam-bath under nitrogen, diacetyl (0·16 g.) was added, and the solution was heated at 60—70° for 30 min. The solution was neutralised with potassium hydrogen carbonate and chilled overnight. The product (0·35 g.) which separated was collected, washed with water, and recrystallised from boiling water, to give *2 : 8-dihydro-4-hydroxy-2-imino-6 : 7 : 8-trimethylpteridine* as yellow needles, decomp. >270°, pK_a 5·85 (imino-group) and 8·90 (hydroxyl group) (Found: C, 53·2; H, 5·0; N, 34·4. $C_9H_{11}ON_5$ requires C, 52·8; H, 5·4; N, 34·2%).

2 : 8-Dihydro-4-hydroxy-2-imino-8-methyl-6 : 7-diphenylpteridine.—2 : 5-Diamino-4-hydroxy-6-methylaminopyrimidine (0·3 g.), acetic acid (3 c.c.), and water (20 c.c.) were heated on the steam-bath, and a solution of benzil (0·42 g.) in ethanol (12 c.c.) was added. The solution was refluxed for 8 hr. during which a bright yellow precipitate slowly separated. This was collected, and recrystallised from dimethylformamide (7 c.c.) to give *2 : 8-dihydro-4-hydroxy-2-imino-8-methyl-6 : 7-diphenylpteridine* (0·04 g.) as yellow prisms, m. p. >300° (Found: C, 66·0; H, 4·3. $C_{19}H_{15}ON_5,H_2O$ requires C, 65·7; H, 4·9%). The infrared spectrum of this material was identical with that of a sample prepared from pyrazine intermediates.[14]

2-Amino-7 : 8-dihydro-4-hydroxy-8-methyl-6 : 7-diphenylpteridine.—2 : 5-Diamino-4-hydroxy-6-methylaminopyrimidine (0·25 g.), benzoin (0·4 g.), acetic acid (2 c.c.), and ethanol (3 c.c.) were

[12] Albert and Goldacre, *J.*, 1946, 706.
[13] Forrest, Hull, Rodda, and Todd, *J.*, 1951, 3.
[14] Dick, Fidler, and Wood, *Chem. and Ind.*, 1956, 1424.

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refluxed for 2 hr., during which a heavy yellow precipitate separated. This was collected and recrystallised from dimethylformamide, to give the 7 : 8-*dihydropteridine* (0·29 g.) as yellow plates, m. p. >300° (Found: C, 68·2; H, 5·2; N, 21·2. $C_{19}H_{17}ON_5$ requires C, 68·8; H, 5·1; N, 21·2%).

2-*Amino*-4-*ethoxy*-6-*methylaminopyrimidine*.—2-Amino-4-chloro-6-methylaminopyrimidine (6·7 g.) [15] and a solution from sodium (1·05 g.) in dry ethanol (60 c.c.) were heated in an autoclave at 130° for 3 hr. The resulting solution was evaporated to dryness *in vacuo*, and the residue crystallised from water (60 c.c.) to give 2-*amino*-4-*ethoxy*-6-*methylaminopyrimidine* as colourless prisms, m. p. 123—126° (Found: C, 49·9; H, 7·2; N, 33·8. $C_7H_{12}ON_4$ requires C, 50·0; H, 7·2; N, 33·3%).

2-*Amino*-5-p-*chlorophenylazo*-4-*ethoxy*-6-*methylaminopyrimidine*.—2-Amino-4-ethoxy-6-methylaminopyrimidine (0·6 g.) in water (8 c.c.), was treated at 0° dropwise with diazotised *p*-chloroaniline (1·1 g.) in N-hydrochloric acid (20 c.c.), then kept at 0° for 5 min., and sodium carbonate (3·5 g.) was added slowly. The product which separated was collected and recrystallised from aqueous acetone to give 2-*amino*-5-p-*chlorophenylazo*-4-*ethoxy*-6-*methylaminopyrimidine* (0·8 g.) as orange needles, m. p. 169—172° (Found: C, 50·9; H. 4·5; N, 27·4. $C_{13}H_{15}ON_6Cl$ requires C, 50·9; H, 4·9; N, 27·4%).

4-*Ethoxy*-2 : 8-*dihydro*-2-*imino*-6 : 7 : 8-*trimethylpteridine*.—The above 5-*p*-chlorophenylazopyrimidine (0·6 g.) was reduced in ethanol (50 c.c.) over Raney nickel in the usual way. The solution was filtered, and acetic acid (2 drops) and diacetyl (0·3 c.c.) were added. The solution was refluxed for 20 min., concentrated *in vacuo* to 5 c.c., and neutralised by saturated potassium hydrogen carbonate solution. The product was collected, and recrystallised from aqueous ethanol (charcoal), to give 4-*ethoxy*-2 : 8-*dihydro*-2-*imino*-6 : 7 : 8-*trimethylpteridine* as red needles, m. p. 178—180° (Found: C, 56·7; H, 6·3; N, 30·4. $C_{11}H_{15}ON_5$ requires C, 56·6; H, 6·5; N, 30·0%). This was not hydrolysed by acid or alkali.

2-*Amino*-4-*methylaminopyrimidine*.—2-Amino-4-chloro-6-methylaminopyrimidine [15] (1·24 g.) was hydrogenated in water (100 c.c.) at room temperature and pressure over freshly hydrogenated 2·5% palladium–charcoal (0·6 g.) in the presence of magnesium oxide (0·9 g.). Theoretical absorption of hydrogen occurred in 12 hr., and no more took place. The mixture was heated to boiling, and the solids were filtered off and washed thoroughly with acetone. 2N-Sodium carbonate (6 c.c.) was added to the combined filtrate and washings, and the mixture was taken to dryness *in vacuo*. The residue was extracted with boiling *iso*butyl methyl ketone (150 c.c.) from which 2-*amino*-4-*methylaminopyrimidine* (0·94 g.) crystallised as colourless needles, m. p. 161—163·5° (Found: C, 48·3; H, 6·5; N, 45·0. $C_5H_8N_4$ requires C, 48·4; H, 6·5; N, 45·2%).

2-*Amino*-5-p-*chlorophenylazo*-4-*methylaminopyrimidine*.—*p*-Chloroaniline (1·4 g.) was diazotised with N-hydrochloric acid (28 c.c.) and sodium nitrite (0·81 g.), and was added to a suspension of 2-amino-4-methylaminopyrimidine (0·94 g.) in water (11 c.c.) at 0°. After 5 min. sodium carbonate (3·5 g.) was added, and the mixture was set aside for 2 hr. at 20°; solid rapidly separated. This was collected and recrystallised from ethanol (30 parts) to give 2-*amino*-5-p-*chlorophenylazo*-4-*methylaminopyrimidine* (2·25 g.) as deep red twisted needles, m. p. 227—229° (Found: C, 50·0; H, 4·3; N, 31·9. $C_{11}H_{11}N_6Cl$ requires C, 50·3; H, 4·2; N, 32·1%).

2 : 8-*Dihydro*-2-*imino*-6 : 7 : 8-*trimethylpteridine*.—2-Amino-5-*p*-chlorophenylazo-4-methylaminopyrimidine (3 g.) in warm methanol (100 c.c.) was hydrogenated over Raney nickel at 4 atm. for 16 hr. The solution was filtered, and used directly for the preparation of the pteridine. Diacetyl (1 c.c.) was added and the solution was refluxed for 30 min., concentrated *in vacuo* to *ca.* 5 c.c., and chilled overnight. The solid (0·5 g.) was collected and recrystallised from methanol (10 parts) to give 2 : 8-*dihydro*-2-*imino*-6 : 7 : 8-*trimethylpteridine* as pale yellow needles, m. p. 235—240° (decomp.), pK_a 5·60 ± 0·1 (Found: C, 57·5; H, 5·4; N, 37·5. $C_9H_{11}N_5$ requires C, 57·2; H, 5·8; N, 37·1%). Ammonia was liberated when the imino-pteridine was heated with concentrated potassium hydroxide solution.

2-*Acetylimino*-2 : 8-*dihydro*-6 : 7 : 8-*trimethylpteridine*.—The above imino-pteridine (0·1 g.) and acetic anhydride (3 c.c.) were heated on the steam-bath for 1 hr., then poured into water (15 c.c.), stirred slowly for 1 hr., and neutralised with sodium hydrogen carbonate solution. The resulting suspension was extracted with chloroform (3 × 50 c.c.), and the extracts, after being washed with water, were taken to dryness *in vacuo*. The residue, crystallised from methanol–ethyl acetate, gave the *acetyl derivative* (0·07 g.) as colourless needles, m. p. 165—170° (Found: N, 30·7. $C_{11}H_{13}ON_5$ requires N, 30·3%).

[15] Imperial Chemical Industries Ltd., B.P. 658,202/1951.

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2 : 8-*Dihydro*-6 : 7 : 8-*trimethyl*-2-*methyliminopteridine*.—2 : 4-Bismethylamino-5-nitropyrimidine (0·6 g.) [16] in ethanol (150 c.c.) was reduced over Raney nickel as above, and to the filtered solution was added diacetyl (0·5 c.c.). The solution was refluxed for 10 min., concentrated to 2 c.c. *in vacuo*, and chilled overnight. The material which separated was recrystallised from methanol–water (10 : 1; 10 parts), to give 2 : 8-*dihydro*-6 : 7 : 8-*trimethyl*-2-*methyliminopteridine* (0·4 g.) as pale buff needles, m. p. 197—198° (decomp.), pK_a 6·1 ± 0·2 (Found: C, 58·9; H, 6·2; N, 34·3. $C_{10}H_{13}N_5$ requires C, 59·2; H, 6·4; N, 34·5%). Methylamine was liberated when the methyliminopteridine was heated with concentrated potassium hydroxide solution.

2 : 4-*Dianilino*-5-*nitropyrimidine*.—2 : 4-Dichloro-5-nitropyrimidine (0·5 g.) [17] in dry benzene (10 c.c.) was added dropwise to a vigorously stirred solution of aniline (4 c.c.) in benzene (10 c.c.). The mixture was stirred for 30 min., and the bright yellow product (1·3 g.) was collected and recrystallised from ethanol (200 parts), to give 2 : 4-*dianilino*-5-*nitropyrimidine* as yellow needles, m. p. 198—202° (Found: C, 63·0; H, 3·99; N, 23·2. $C_{16}H_{13}O_2N_5$ requires C, 62·6; H, 4·25; N, 22·8%).

2 : 8-*Dihydro*-6 : 7 : 8-*triphenyl*-2-*phenyliminopteridine*.—2 : 4-Dianilino-5-nitropyrimidine (0·3 g.) in ethanol (200 c.c.) was reduced over Raney nickel in the usual way. To the filtered solution were added benzil (0·3 g.), acetic acid (0·3 c.c.), and water (3 c.c.). The solution was heated on the steam-bath for 20 min. and then concentrated *in vacuo* to 10 c.c. and chilled overnight. The product which separated was collected and recrystallised from ethanol (100 parts), to give 2 : 8-*dihydro*-6 : 7 : 8-*triphenyl*-2-*phenyliminopteridine* (0·25 g.) as pale green plates, m. p. 225—227° (decomp.) (Found: C, 78·1; H, 4·9; N, 15·3. $C_{30}H_{21}N_5$ requires C, 79·8; H, 4·6; N, 15·5%). This gave a deep green colour in concentrated sulphuric acid.

2 : 8-*Dihydro*-6 : 7-*dimethyl*-8-*phenyl*-2-*phenyliminopteridine*.—2 : 4-Dianilino-5-nitropyrimidine (0·4 g.) was reduced and condensed with diacetyl as above to give 2 : 8-*dihydro*-6 : 7-*dimethyl*-8-*phenyl*-2-*phenyliminopteridine* (0·15 g.) as pale pink needles (from ethanol), m. p. 241—242° (decomp.) (Found: C, 73·9; H, 5·3; N, 21·8. $C_{20}H_{17}N_5$ requires C, 73·4; H, 5·2; N, 21·5%).

Potentiometric Titrations.—Weighed quantities of the pteridines (approx. M/1000; 5 mg.) were dissolved in 25 c.c. of distilled water and titrated with 0·1M-hydrochloric acid or -sodium hydroxide in a cell containing a glass electrode calibrated by means of phthalate and borate buffers. The reference electrode was a calomel half-cell immersed in the solution. A Cambridge pH meter was used for measurement of pH values. The solution was stirred by a current of nitrogen, and the titrant was added from a micrometer syringe, about fifteen small additions being made. The pK_a values were calculated according to the equation $pK_a = pH - \log\{([B] + [H^+])/([BH^+] - [H^+])\}$ where [B], [BH^+], and [H^+] are the calculated concentrations of the base, conjugate acid, and hydrogen ion, corrected for the dilution caused by addition of acid or alkali.

The authors thank Dr. D. C. Munro for helpful discussion of this and the preceding paper. They are also grateful to Dr. A. C. Syme and Mr. Wm. McCorkindale for the microanalyses and to Dr. G. T. Newbold and Miss Norma Caramando for the infrared spectra.

The Royal College of Science and Technology, Glasgow. [*Received, April 4th*, 1957.]

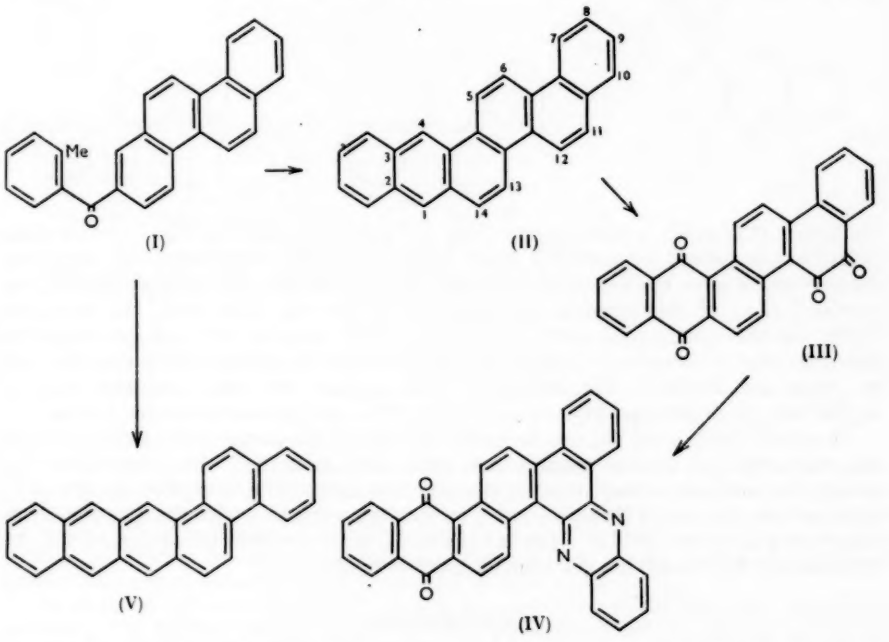
[16] Brown, *J. Appl. Chem.*, 1954, **4**, 72.
[17] *Idem, ibid.*, 1952, **2**, 239.

836. 2 : 3-*Benzopicene and Naphtho*(2′ : 3′-1 : 2)*chrysene.*

By E. Clar and W. Kelly.

2 : 3-Benzopicene was obtained from a mixture of *o*-toluoylchrysenes, which were prepared by a reaction of *o*-toluoyl chloride, chrysene, and aluminium chloride under drastic conditions. Naphtho(2′ : 3′-1 : 2)chrysene can be easily obtained from the quinone (X) by reduction with zinc dust in pyridine and acetic acid. The oxygen-containing product from the zinc dust melt of the quinone (X) is not the anthrone derivative (XI) as claimed by Beyer and Richter but the cyclic epoxy-compound (VIII).

Chrysene reacts in the Friedel–Crafts reaction under mild conditions in position 2. However, if the reaction with *o*-toluoyl chloride in tetrachloroethane is carried out at 95° a mixture of ketones is formed, which after pyrolysis at 400° yields a mixture of hydrocarbons. This consists of a yellow hydrocarbon (absorption bands in benzene at 4720 and 4420 Å) and a pale yellow hydrocarbon (first band at 4040 Å). Complete chromatographic separation was not achieved and the yellow hydrocarbon could not be obtained pure. It was therefore removed from the mixture by a cautious treatment with maleic anhydride

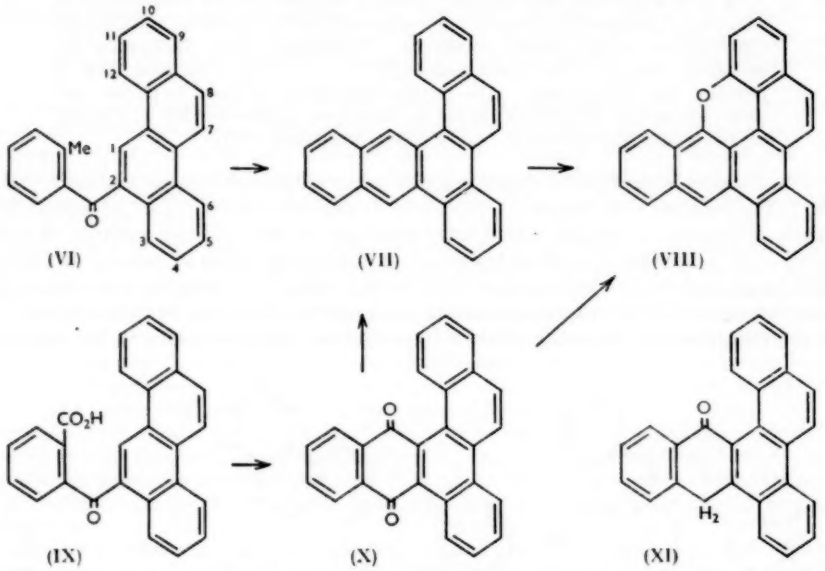


until its absorption bands disappeared. From its higher reactivity and the position of its absorption bands near to the red it might be concluded that it has the structure (V) of a naphthotetracene. This is the only system with four linearly condensed rings which could be formed in this synthesis.

The less reactive pale yellow hydrocarbon gave a diquinone when oxidised with chromic anhydride in acetic acid. This has two *o*-carbonyl groups since it formed a phenazine derivative (IV) with *o*-phenylenediamine. The two carbonyl groups of the *o*-quinone complex cannot be in positions 5 and 6 because treatment with hydrazine hydrate does not

produce an azine involving positions 4 and 5. Thus the most likely structure of the diquinone is that given in formula (III), chrysene having reacted at position 4 or 3.

During pyrolysis of the ketone mixture an oxygen-containing product was obtained besides the two hydrocarbons mentioned above. This compound obviously originated from



the ketone (VI) which is pyrolysed to (VII) and then oxidised to (VIII). The structure (VIII) was confirmed by synthesis from chrysene, phthalic anhydride, and aluminium chloride which gave the keto-acid (IX) and, by ring closure with benzoyl chloride, the quinone[1] (X). If this quinone was submitted to the zinc dust melt, the compound (VIII) was obtained in good yield. Compound (VIII) contains two hydrogen atoms less than indicated by formula (XI) which was attributed to the product of the zinc dust melt by Beyer and Richter.[2] The structure (VIII) explains why this compound does not enolise with alkali, does not give an acetyl derivative, and cannot be reduced further.

However, the quinone (X) can be readily reduced to the parent hydrocarbon (VII) by reduction with zinc dust in pyridine and acetic acid, a method which avoids the high temperature and condensing action of the zinc dust melt. The absorption spectra of the hydrocarbons (II) and (VII) are recorded in the Figure together with the spectrum of the oxygen-ring compound (VIII). The last shows the strong red shift in comparison with the hydrocarbon (VII) which has also been observed in similar cases.[3]

Experimental

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

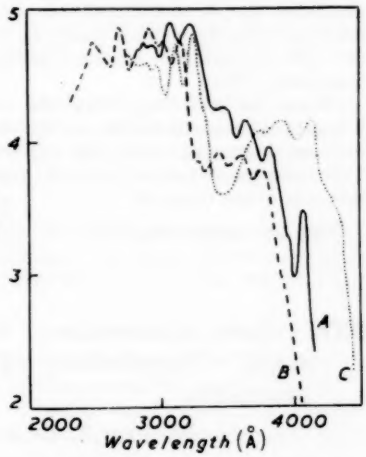
Condensation of Chrysene with o-Toluoyl Chloride.—Powdered aluminium chloride (60 g.) was added during 4 min. to a mixture of chrysene (46 g.) and *o*-toluoyl chloride (33 g.) in tetrachloroethane (60 ml.) at 95° and stirred for a further 5 min. The orange-red mixture was cooled, decomposed, and diluted with more tetrachloroethane. The organic layer was washed

[1] I.G. Farbenind. A.-G., G.P. 652,912; Ges. Chem. Ind. in Basel, Swiss P. 179,440; *Chem. Zentr.*, 1936, I, 2637; 1938, I, 2064.
[2] Beyer and Richter, *Ber.*, 1940, **73**, 1319.
[3] Clar, *Ber.*, 1940, **73**, 351; Clar, Kelly, Stewart, and Wright, *J.*, 1956, 2652.

successively with hot dilute hydrochloric acid, hot dilute aqueous ammonia, and hot water. The tetrachloroethane was distilled off and the residue pyrolysed at about 400° for 15 min., to give a black solid (56 g.). 28 g. of this were sublimed in a vacuum. Fractions were collected between 170° and 340° during 45 hr. The initial fractions (collected at 170—220°) were mainly unchanged chrysene. The later fractions (13 g.) were collected together and extracted with 150 ml. of warm benzene.

2 : 3-*Benzopicene* (II).—The residue (4·2 g.) from the above benzene extraction was recrystallised from xylene, giving yellow plates (1·8 g.). Spectroscopy (bands at 4720, 4420, and 4040 Å) showed the plates to be a mixture of two compounds. Attempts to separate them by chromatography were unsuccessful. Several recrystallisations from 1 : 2 : 4-trichlorobenzene containing small quantities of maleic anhydride gave pale yellow plates, m. p. 394—395°, of the *benzopicene* (Found: C, 95·3; H, 5·1. $C_{26}H_{16}$ requires C, 95·1; H, 4·9%). The compound did not dissolve in concentrated sulphuric acid and had a blue fluorescence in xylene solution.

15-*Oxatribenzo*[a,e,jk]*pyrene* (VIII).—The above benzene extract was chromatographed on alumina with benzene as eluant. A first small colourless band gave a small quantity of chrysene. A second yellow band yielded yellow needles, m. p. 288—289° (Beyer and Richter,[3] 285—286°), of the 15-*oxatribenzopyrene* (Found: C, 91·0; H, 4·2. $C_{26}H_{14}O$ requires C, 91·2; H, 4·1%). The compound was identical with that obtained as below by the reduction of naphtho(2′ : 3′-1 : 2)chrysene-1′ : 4′-quinone, and dissolved in concentrated sulphuric acid to a deep red solution.



Absorption spectrum of (*A*) 2 : 3-*benzopicene* (II) *in* C_6H_6 [max. (Å; log ε in parentheses): 4055 (3·46); 3820 (3·96), 3630 (4·15), 3470 (4·26); 3245 (4·88), 3110 (4·89), 2980 (4·74)], (*B*) *naphtho*(2′ : 3′-1 : 2)-*chrysene* (VII) *in* EtOH [max. 3760 (3·77), 3610 (3·89), 3460 (3·91), 3280 (3·85); 3150 (4·74), 3020 (4·75); 2920 (4·84), 2700 (4·84), 2490 (4·75)], *and* (*C*) *of* 15-*oxatribenzo*[a,e,jk]*pyrene* (VIII) *in* C_6H_6 [max. 4140 (4·15), 3910 (4·15), 3720 (4·07); 3260 (4·81), 3115 (4·73), 2980 (4·56), 2890 (4·58)].

2 : 3-*Benzopicene*-1 : 4-11 : 12-*diquinone* (III).—Chromium trioxide (0·26 g.) in water (1 ml.) was added to a suspension of benzopicene (0·1 g.) in acetic acid (6 ml.) After 3 hr. under reflux the suspension was filtered and the orange powder crystallised from nitrobenzene as orange feathery needles of the *diquinone*, m. p. 387—388° (Found: C, 80·6; H, 3·5. $C_{26}H_{12}O_4$ requires C, 80·4; H, 3·1%). The compound gave an orange vat with alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a reddish-brown solution.

An excess of hydrazine hydrate was added to a suspension of the diquinone (III) in hot pyridine. The reddish-orange suspension changed to deep red and the diquinone dissolved completely. The solution was heated under reflux for 20 min. and the pyridine was concentrated to small bulk but no crystallisation took place. The light brown precipitate, formed on addition of water and boiling, crystallised from nitrobenzene as orange needles identical with the benzopicenediquinone (III).

An excess of *o*-phenylenediamine (10 mg.) and the diquinone (III) (14 mg.) in nitrobenzene (3 ml.) were heated under reflux for 30 min. The dark yellow crystals (13 mg.) obtained were recrystallised from nitrobenzene, to give fine yellow needles, m. p. 363—364°, of the *phenazine* (IV) (Found: N, 5·9. $C_{32}H_{16}O_2N_2$ requires N, 6·1%). The compound gave an orange-red vat in alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a violet-red solution.

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2-o-*Carboxybenzoylchrysene* (IX).—Powdered aluminium chloride (117 g.) was added, during 5 min., to phthalic anhydride (64 g.) and chrysene (80 g.) in tetrachloroethane (200 ml.) at 90°. The mixture became reddish-orange and the temperature rose to 98°. The reaction quickly subsided and, after decomposition, the tetrachloroethane layer was separated and washed with hot dilute hydrochloric acid and hot water. The tetrachloroethane solution was extracted with rather concentrated ammonia solution which precipitated an ammonium salt. Acidification of this salt gave an acid (80 g.) which on being recrystallised several times from acetic acid gave colourless needles, m. p. 206—211° (Beyer and Richter,[2] m. p. 213—214°), of 2-*o*-carboxybenzoylchrysene. The mother-liquor from the ammonium salt, on acidification, yielded another portion of acid product (24 g.) (Found: C, 82·8; H, 4·6. Calc. for $C_{26}H_{16}O_3$: C, 83·0; H, 4·3%).

Naphtho(2′ : 3′-1 : 2)*chrysene*-1′ : 4′-*quinone* (X).—A solution of 2-*o*-carboxybenzoylchrysene (60 g.) in benzoyl chloride (180 ml.) was heated under reflux. Concentrated sulphuric acid was added dropwise at intervals until a transient blue colour no longer appeared. The solution was boiled for a further 10 min. Orange needles (23 g.) crystallised from the solution on cooling. Recrystallisation from xylene gave orange needles, m. p. 273—274°, of the quinone.

Naphtho(2′ : 3′-1 : 2)*chrysene* (VII).—The quinone (X) (5 g.), zinc dust (5 g.), and pyridine (70 ml.) were heated under reflux and 80% acetic acid (80 ml.) was added during 5 hr. The initial deep orange-red solution changed through pale orange to a yellowish-green. The pyridine solution was filtered into water, and the precipitate was heated above its m. p. in a vacuum, powdered, and chromatographed in benzene on alumina with benzene as eluant. A first colourless band yielded colourless plates, m. p. 187—188° (Beyer and Richter,[2] 185—186°), of naphtho(2′ : 3′-1 : 2)chrysene. A second yellow band yielded yellow needles, m. p. 288—289°, of the compound (VIII).

When the acid (24 g.) from the mother-liquor of the crystallised ammonium salt of the 2-*o*-carboxybenzoylchrysene was cyclised and the mixture of the quinones reduced as above a mixture of benzopicene (II) and naphthotetracene (V) (identified by its spectrum) was obtained. This indicates that under the latter condition described some phthalic anhydride reacts with a side ring of the chrysene.

THE UNIVERSITY, GLASGOW. [*Received, April 15th*, 1957.]

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837. *Cyclic Keto-amines. Part II.* The Preparation and Spectroscopic Characteristics of Substituted* 1 : 2 : 3 : 4-*Tetrahydro*-4-*oxoquinolines.*

By JOHN T. BRAUNHOLTZ and FREDERICK G. MANN.

A number of new substituted 1 : 2 : 3 : 4-tetrahydro-4-oxoquinolines has been prepared; the standard cyclisation procedures are found to be more widely applicable than hitherto reported. The infrared and ultraviolet spectra of these compounds are discussed in relation to their structures.

THE synthesis of 1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline (II; R = R′ = R″ = H) and certain simple derivatives was first described by Clemo and Perkin;[1] β-(toluene-*p*-sulphonanilido)-propionic acids of type (I; R″ = SO_2·C_6H_4Me, R‴ = OH) were either converted into their acid chlorides and cyclised by phosphorus oxychloride, or were cyclised directly with phosphoric anhydride, and hydrolytic removal of the protecting toluene-*p*-sulphonyl group then gave the parent keto-amines. This route has been followed by other workers [2,3] and gives good yields of various *Bz*-substituted 1 : 2 : 3 : 4-tetrahydro-4-oxoquinolines. A second route involves the monocyclisation of various *NN*-biscyanoethyl derivatives of

* Ittyerah and Mann, *J.*, 1956, 3179, is to be regarded as Part I of this series.

[1] Clemo and Perkin, *J.*, (*a*) 1924, **125**, 1608; (*b*) 1925, **127**, 2297.
[2] Johnson, Woroch, and Buell, *J. Amer. Chem. Soc.*, 1949, **71**, 1901.
[3] Elderfield, Gensler, Bembry, Kremer, Brody, Hageman, and Head, *ibid.*, 1946, **68**, 1259; Elderfield and Maggiolo, *ibid.*, 1949, **71**, 1906.

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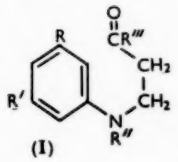
aromatic amines to give quinolines of type (II; R″ = $[CH_2]_2 \cdot CO_2H$ or $[CH_2]_2 \cdot CN$),[4,5] which in boiling hydrochloric acid lose the 2-carboxyethyl group to form the corresponding quinolines (II; R″ = H).[4] Another cyclisation route has been used by Bekhli,[6] who converted the acid (III) into the quinoline (II; R = H, R′ = Cl, R″ = Ac) by the action of acetic anhydride and potassium acetate.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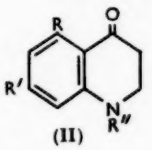
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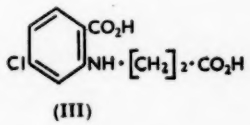

(III)

As a preliminary to work designed to lead to analogous systems containing a seven-membered keto-amine ring (see following paper), the synthesis of new ketones of type (II) containing the activating methoxyl group, and the influence of the acyl group R″ on the course of the cyclisation were investigated.

Methyl β-arylaminopropionates were readily obtained by addition of methyl acrylate to aromatic primary amines in the presence of acetic acid,[2] and then converted by the usual steps into the *N*-acylated amino-acids (I; R″ = SO_2Ph, $SO_2 \cdot C_6H_4Me$, Bz, or Ac, R‴ = OH) suitable for cyclisation.

We find, not unexpectedly, that the Friedel–Crafts procedure converts the benzenesulphonyl compound (I; R = R′ = H, R″ = SO_2Ph, R‴ = OH) into the 1-benzenesulphonyl-1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline (II; R = R′ = H, R″ = SO_2Ph) in good yield, similar to that obtained for the toluene-*p*-sulphonyl analogue (II; R = R′ = H, R″ = $SO_2 \cdot C_6H_4Me$).

Previous workers [3] had stressed that the presence of the *N*-toluene-*p*-sulphonyl group in acids of type (I) was apparently essential for cyclisation. We have therefore briefly examined the behaviour of the acids (I; R = R′ = H, R″ = Ac or Bz, R‴ = OH) under similar conditions.

β-*N*-Acetanilidopropionic acid (I; R = R′ = H, R″ = Ac, R‴ = OH) was converted by thionyl chloride into the acid chloride, but attempted cyclisation of the latter under various conditions gave intractable tars, having an almost negligible ketonic content. On the other hand, the acid chloride of the analogous *N*-benzoyl-acid, when treated with aluminium chloride, gave two distinct types of ketone according to the solvent employed. When dissolved in benzene at room temperature, it reacted with the solvent to form the β-substituted propiophenone (I; R = R′ = H, R″ = Bz, R‴ = Ph) in good yield: the constitution of this compound was confirmed by its infrared spectrum, which showed strong sharp bands at 1675 (conjugated C:O) and at 1629 cm.$^{-1}$ (tertiary amide). In boiling chlorobenzene, the ketone (I; R = R′ = H, R″ = Bz, R‴ = C_6H_4Cl) was similarly obtained.

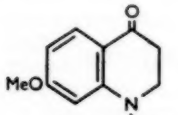
The chloride, when treated however with aluminium chloride in carbon disulphide at room temperature, underwent cyclisation to form 1-benzoyl-1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline (II; R = R′ = H, R″ = Bz), identical with that which Clemo and Perkin [1] obtained by benzoylation of the parent oxoquinoline (II; R = R′ = R″ = H). The infrared spectrum of this compound showed bands at 1682 (conjugated cyclic C:O) and at 1642 cm.$^{-1}$ (tertiary amide).

These results show that the presence of the *N*-benzoyl group in chlorides of the acids of type (I) deactivates the benzene ring for cyclisation purposes to a much greater extent

[4] Braunholtz and Mann, *J.*, 1952, 3046.
[5] *Idem*, *J.*, 1954, 651; Johnson and DeAcetis, *J. Amer. Chem. Soc.*, 1953, **75**, 2766.
[6] Bekhli, *Doklady Akad. Nauk S.S.S.R.*, 1955, **101**, 679; *Chem. Abs.*, 1956, **50**, 3441.

than does the *N*-arylsulphonyl group, and subsequently promotes direct reaction with an aromatic solvent.

In order to promote the desired cyclisation by activation of the benzene ring, we have prepared from *m*-anisidine the acids (I; R = H, R′ = OMe, R″ = SO_2Ph and $SO_2{\cdot}C_6H_4Me$, R‴ = OH). The chloride of the first acid in benzene solution gave solely the quinolone (IV), but that of the second gave two isomeric quinolones, (V), m. p. 104—105°, and (VI), m. p. 114°, in almost equal quantities.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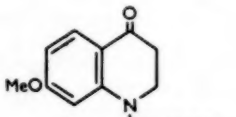
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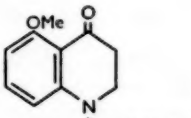
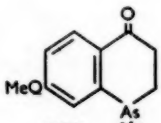

(VI)


(VII)

It is noteworthy that, from similar cyclisations, 1 : 2 : 3 : 4-tetrahydro-7-methoxy-1-methyl-4-oxoarsinoline [7] (VII) and the quinolone [2] (II; R = H, R′ = Cl, R″ = $SO_2{\cdot}C_6H_4Me$) have been isolated without accompanying isomers, whereas the acid (I; R = H, R′ = Me, R″ = $SO_2{\cdot}C_6H_4Me$, R‴ = OH) gave rise to both the quinolones (II; R = H, R′ = Me, R″ = $SO_2{\cdot}C_6H_4Me$) and (II; R = Me, R′ = H, R″ = $\cdot SO_2{\cdot}C_6H_4Me$), the former being isolated in much greater yield than the latter.[1b]

Spectroscopic evidence described below provides support for the allocation of structures (IV), (V), and (VI).

(*a*) The infrared spectra, in the region 880—690 cm.$^{-1}$, of the quinolones (IV), (V), and (VI), and of certain related compounds, are summarised in Table 1. The band systems of the quinolone (IV) and its *Bz*-unsubstituted analogue (II; R = R′ = H, R″ = SO_2Ph) in the region 690—790 cm.$^{-1}$ correspond very closely in both position and relative intensities; it is therefore possible, without detailed assignment of these bands, to correlate the additional absorption at 863 cm.$^{-1}$ in the spectrum of (IV) with a 1 : 2 : 4-pattern of nuclear substitution, for which a " normal " range of 860—800 cm.$^{-1}$ has been suggested.[8]

In the infrared spectra of the isomers (V) and (VI), absorption bands at 822 and 817 cm.$^{-1}$ respectively may be assigned to the toluene-*p*-sulphonyl group by comparison with that of the quinolone (II; R = R′ = H, R″ = $SO_2{\cdot}C_6H_4Me$), in which the corresponding absorption is at 817 cm.$^{-1}$. The proposed structure (V) for the less soluble isomer is

TABLE 1. *Infrared spectra of the tetrahydro-4-oxoquinolines in the region* 880—690 *cm.*$^{-1}$ *in Nujol mull.**

(II; R = R′ = H, R″ = $SO_2{\cdot}C_6H_4Me$) ...	834 (m)	817 (m)	779 (s)	735 (s)	687 (s)
(II; R = R′ = H, R″ = SO_2Ph)	835 (m)	787 (s)	767 (m)	738 (m)	694 (m)
(IV)	863 (m)	784 (s)	765 (m)	728 (s)	695 (m)
(V)	875 (m)	822 (m)	777 (s)	710 (m)	690 (s)
(VI)	850 (m)	817 (s)	790 (m)	698 (s)	

* m and s indicate medium and strong bands respectively.

supported by an absorption band at 875 cm.$^{-1}$, close to that characterising the 1 : 2 : 4-trisubstituted system of the quinolone (IV); absorption at 790 cm.$^{-1}$ in the spectrum of the more soluble quinolone (VI) corresponds to the 1 : 2 : 3-trisubstituted aromatic nucleus.

(*b*) Decisive interpretation of the infrared spectra of the quinolones (V) and (VI) in the 880—790 cm.$^{-1}$ region is, however, complicated by the polar groups present. Confirmation of the structural assignments has therefore been sought from ultraviolet absorption studies designed to detect interaction between the carbonyl group (or a derivative of this group) and a methoxyl group *ortho* to it. Table 2 shows that, although the spectra of

[7] Mann and Wilkinson, *J.*, 1957, 3336.
[8] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1956 pp. 54 ff.

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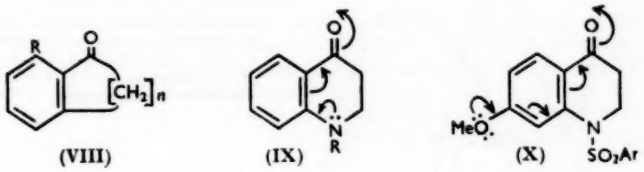
quinolones of type (II) are considerably modified by the introduction of a methoxyl group, they do not afford evidence for such steric effects; similar insensitivity to *ortho*-substitution has also been discovered in the case of certain cyclanones [9] (*e.g.*, VIII; $n = 3$), although the ultraviolet spectra of *ortho*-substituted acetophenones are appreciably modified.

TABLE 2. *Ultraviolet absorption spectra of the tetrahydro-4-oxoquinolines and their derivatives in ethanol* (ε *in parentheses*).

Compound	$\lambda_{max.}$	$\lambda_{min.}$	$\lambda_{inf.}$
(II; R = R′ = H, R″ = SO_2Ph)	319 (2,700)	285—286 (840)	236—240 (15,500)
	219—220 (20,600)		256—260 (9,990)
(IV)	281 (13,900)	277—278 (13,800)	
	275 (13,900)	270 (12,600)	
	252—253 (18,000)	233—235 (13,000)	
	217—218 (17,300)		
(V)	277 (14,620)	270—271 (13,740)	
	254 (19,710)	238—239 (11,070)	
	225 (19,470)		
(VI) *	278, 255, 225	268, 240	
2 : 4-Dinitrophenylhydrazone of (V) ...	392 (33,600)	324 (5,800)	302—294 (10,980)
	218—219 (37,300)		256—246 (25,550)
2 : 4-Dinitrophenylhydrazone of (VI)...	392 (29,700)	325 (4,740)	304—284 (10,900)
	218 (32,000)	210—209 (29,700)	258—250 (21,500)

* Owing to the very small quantity of material available, the ε values are not accurately comparable with those in other spectra, and are omitted.

When however the ketones (V) and (VI) are converted into their 2 : 4-dinitrophenylhydrazones, appreciable differences in ε values become apparent; the allotted structures are thereby supported, since the derivative with the less intense absorption maxima will be the one in which a weak *ortho*-effect causes partial steric inhibition of resonance.



(VIII) (IX) (X)

In earlier papers [10] concerning cyclic keto-amines of type (II) or of analogous structure, we have correlated the colour (and fluorescence) of their solutions with nitrogen–carbonyl interaction as shown in (IX). The more precise spectroscopic evidence now given in the Figure demonstrates the predicted hypsochromic shift of the long-wavelength absorption maximum when electron-release by nitrogen is reduced by the substituent R. It is noteworthy that the highest-wavelength absorption maximum of the arsinolone (VII), in which arsenic–carbonyl interaction is probably negligible, occurs at 281 mμ (ε 14,000),[7] that of α-tetralone (VIII; R = H, $n = 3$) being at 248 mμ (ε 12,200).[11]

The corresponding carbonyl absorption frequencies in the infrared spectra of the quinolones are summarised in Table 3. If the carbonyl band at 1681 cm.$^{-1}$ for α-tetralone [12] (liquid) (VIII; R = H, $n = 3$) is taken as a standard, nitrogen–carbonyl interaction in the quinolones (II; R = R′ = H, R″ = Me or Ph) leads to a " frequency " decrease of 4 cm.$^{-1}$; when this interaction is suppressed by acylation of the amine group, the resulting keto-amines show carbonyl absorption at higher frequencies, close to the normal α-tetralone value. When, however, the methoxyl group is introduced into these acylated quinolones

[9] Hedden and Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 3744.
[10] *E.g.*, Braunholtz and Mann, *J.*, 1953, 1817.
[11] Schubert and Sweeney, *J. Amer. Chem. Soc.*, 1955, **77**, 2297.
[12] *Idem*, *ibid.*, p. 4172.

(as in IV, V, and VI), its interaction with the carbonyl group (see X) now reduces the carbonyl absorption to almost the same value as that produced by the amine–carbonyl interaction in the quinolones (II; R = R′ = H, R″ = Me or Ph). The appreciable variation (6 cm.$^{-1}$) between the (C:O) bands for the isomeric toluene-*p*-sulphonyl ketones

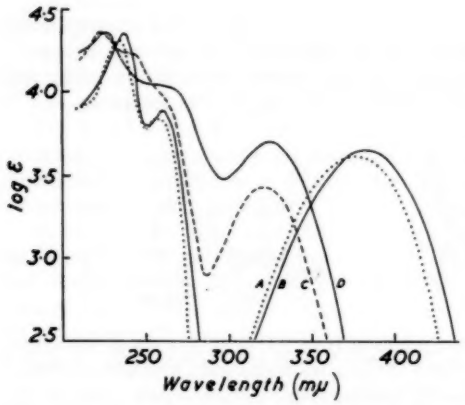
TABLE 3. *Infrared spectra of the tetrahydro-4-oxoquinolines* (II) *in the region* 1650—1700 *cm.*$^{-1}$ (*in Nujol except as stated*).

R	R′	R″	ν_{CO} (cm.$^{-1}$)	R	R′	R″	ν_{CO} (cm.$^{-1}$)
H	H	Ph	1677	H	H	$SO_2{\cdot}C_6H_4Me$	1685
*H	H	Me	1677	H	OMe	SO_2Ph	1675
H	H	Bz	1682	H	OMe	$SO_2{\cdot}C_6H_4Me$	1676
H	H	SO_2Ph	1683	OMe	H	$SO_2{\cdot}C_6H_4Me$	1670

* Liquid film.

(V) and (VI) has apparently the same structural significance as the difference in the ν_{CO} values of *o*-methoxyacetophenone (1649 cm.$^{-1}$, liquid) and *p*-methoxyacetophenone (1657 cm.$^{-1}$, liquid).[13]

The spectroscopic results discussed above provide clear evidence for partial nitrogen–carbonyl interaction of the amide type, but this is not sufficiently powerful to destroy the normal ketonic and (where applicable) basic reactivities of such systems. It is to be



Ultraviolet spectra, in ethanol, of (*A*) 1 : 2 : 3 : 4-*tetrahydro-4-oxoquinoline,* (*B*) 1 : 2 : 3 : 4-*tetrahydro-1-methyl-4-oxoquinoline,* (*C*) 1 : 2 : 3 : 4-*tetrahydro-4-oxo-1-toluene-p-sulphonylquinoline, and* (*D*) 1-*benzoyl*-1 : 2 : 3 : 4-*tetrahydro-4-oxoquinoline.*

expected, moreover, that any steric factor reducing coplanarity of the carbonyl and amino-groups and the aromatic ring system should enhance these normal properties; this factor is of importance in the study of analogous seven-membered ring systems described elsewhere [14] (see also following paper).

EXPERIMENTAL

Addition of Methyl Acrylate to Aromatic Primary Amines. Methyl β-Anilinopropionate (I; R = R′ = R″ = H, R‴ = OMe).—This ester was prepared essentially by the method of Johnson *et al.*[3] A mixture of aniline (100 c.c.), methyl acrylate (110 c.c., 1·25 mols.), and acetic acid (10 c.c.) was heated under reflux for 8 hr., and then distilled under reduced pressuer, giving the fractions, (*a*) b. p. 60—125°/2 mm. (3 g.), (*b*) b. p. 132°/2·5 mm. (140 g.), and (*c*) b. p. 160—170°/3 mm. (*ca.* 10 g.), and a residue of undistillable polymer. Fraction (*b*) crystallised

[13] Hergert and Kurth, *ibid.*, 1953, **75**, 1622.
[14] Braunholtz and Mann, *Chem. and Ind.*, 1957, 266.

readily, giving methyl β-anilinopropionate, m. p. 38° (75% yield), sufficiently pure for subsequent work.

Methyl β-m-*methoxyphenylpropionate.* A mixture of *m*-anisidine (25 g.), methyl acrylate (18 g., 1 mol.), and acetic acid (5 c.c.), when heated under reflux for 12 hr. gave on distillation solely the *ester*, b. p. 165—167°/1 mm. (31 g., 75%) (Found: N, 6·8. $C_{11}H_{15}O_3N$ requires N, 6·7%). This ester gave no precipitate with methanolic picric acid.

N-*Acyl*-β-*arylaminopropionic Acids.*—N-*Acetyl*-β-*anilinopropionic acid* (I; R = R′ = H, R″ = Ac, R‴ = OH). Attempts to acetylate the methyl ester (I; R = R′ = R″ = H, R‴ = OMe) by acetic acid–acetic anhydride under reflux were unsatisfactory. A solution of the ester (17·9 g.) in dry benzene (50 c.c.) was therefore treated (in alternate portions, with shaking) with acetyl chloride (7·9 g.) and pyridine (7·9 g.). After 30 min., the mixture was shaken with water and aqueous sodium carbonate. The benzene layer on evaporation left a pale straw-coloured mobile syrup, which was dissolved in methanol (150 c.c.) and 10% aqueous potassium hydroxide (50 c.c.) and set aside at room temperature for 20 hr. The solution was acidified and evaporated under reduced pressure; the residual syrup slowly crystallised when triturated with water, affording the *acid*, m. p. 108° from water (10 g., 50%) (Found: C, 64·1; H, 6·3; N, 6·6. $C_{11}H_{13}O_3N$ requires C, 63·8; H, 6·3; N, 6·8%).

N-*Benzoyl*-β-*anilinopropionic acid.* The methyl ester (I; R = R′ = R″ = H, R‴ = OMe) (17·9 g.) was shaken with benzoyl chloride (14 g., 1 mol.) and 10% aqueous sodium hydroxide (100 c.c.) for 1 hr., the temperature being allowed to rise to 50°. The mixture when acidified deposited an oil which ultimately crystallised, and was partially purified by reprecipitation from aqueous sodium carbonate solution. Recrystallisation from benzene gave the *acid*, m. p. 84—87° (20 g., 74%) (Found: C, 71·5; H, 5·6; N, 5·2. $C_{16}H_{15}O_3N$ requires C, 71·4; H, 5·6; N, 5·2%).

Repetition of this experiment at 15—20° gave a granular solid before acidification; this was collected, and addition of hydrochloric acid to the filtrate precipitated the acid (I; R = R′ = H, R″ = Bz, R‴ = OH) (9 g.), as before. The granular solid was the *methyl ester* (I; R = R′ = H, R″ = Bz, R‴ = OMe), m. p. 77·5—78·5° after crystallisation from aqueous methanol (13 g.) (Found: C, 72·3; H, 6·3; N, 5·0. $C_{17}H_{17}O_3N$ requires C, 72·3; H, 6·05; N, 4·95%).

N-*Benzenesulphonyl*-β-*anilinopropionic acid.* The ester (17·9 g.) was shaken with benzenesulphonyl chloride (17·7 g., 1 mol.) and 10% aqueous sodium hydroxide (100 c.c.). Acidification gave a heavy syrup which was separated, washed with water, and then dissolved in methanol (150 c.c.) containing 10% aqueous potassium hydroxide (50 c.c.) and set aside for 16 hr. to complete the hydrolysis. Acidification then afforded the *acid*, m. p. 115° (from benzene–*cyclo*hexane) (10 g., 33%) (Found: C, 59·1; H, 4·5; N, 4·55. $C_{15}H_{15}O_4NS$ requires C, 59·0; H, 4·9; N, 4·6%).

N-Toluene-*p*-sulphonyl-β-anilinopropionic acid was prepared in 80% yield from the ester by the method of Johnson *et al.*,[2] and had m. p. 144—146° after crystallisation from benzene.

N-*Benzenesulphonyl*-β-m-*methoxyphenylpropionic acid.* The ester (I; R = R″ = H, R′ = R‴ = OMe) (10 g.) was treated with benzenesulphonyl chloride (10 g.) precisely as the ester (I; R = R′ = R″ = H, R‴ = OMe). The solution of the oil in alkali–methanol was acidified after 20 hr.; the precipitated viscous syrup solidified after trituration with water, methanol, and benzene. Recrystallisation from benzene gave the *acid*, m. p. 118° (10 g., 30%) (Found: C, 57·1; H, 5·0; N, 4·3. $C_{16}H_{17}O_5NS$ requires C, 57·3; H, 5·1; N, 4·2%).

N-*Toluene*-p-*sulphonyl*-β-m-*methoxyphenylpropionic acid* (I; R = H, R′ = OMe, R″ = SO_2·C_6H_4Me, R‴ = OH) similarly prepared, formed needles, m. p. 112—113°, from benzene–*cyclo*hexane (Found: C, 58·6; H, 5·3; N, 3·8. $C_{17}H_{19}O_5NS$ requires C, 58·4; H, 5·5; N, 4·0%): 30% yield.

Characterisation of Acid Chlorides.—In the case of the acids (I; R = R′ = H, R″ = Ac or Bz, R‴ = OH) where subsequent cyclisation might be difficult, evidence was required that the intermediate acid chloride was formed in high yield. A solution of each acid (1 g.) in benzene (10 c.c.) containing thionyl chloride (1 c.c.) was heated under reflux for 30 min. Volatile constituents were removed first by heat under reduced pressure, and then by several co-distillations with small quantities of benzene. A benzene solution of the residual syrup, when treated with *p*-toluidine (1 g.), deposited *p*-toluidine hydrochloride almost quantitatively. The filtrate from the first acid gave a viscous syrup: that from the second acid readily afforded N-*benzoyl*-β-*anilinopropiono*-p-*toluidide* (I; R = R′ = H, R″ = Bz, R‴ = NH·C_6H_4Me),

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m. p. 134—135° (from ethanol) (1·2 g., 90%) (Found: C, 77·3; H, 6·2; N, 7·7. $C_{23}H_{22}O_2N_2$ requires C, 77·1; H, 6·2; N, 7·8%).

Friedel–Crafts Condensations of Acid Chlorides.—The acid (unless otherwise stated) was converted into the chloride by the above method.

(i) N-*Acetyl*-β-*anilinopropionic acid.* Attempts to cyclise the chloride were inconclusive. A benzene solution when treated with a small excess of aluminium chloride at room temperature darkened and yielded only a trace of ketonic material.

(ii) N-*Benzoyl*-β-*anilinopropionic acid.* (*a*) The acid (5 g.) was converted into the chloride which was treated in benzene at 0° with powdered aluminium chloride (5 g.); there was considerable evolution of hydrogen chloride. The mixture was set aside at room temperature for 20 hr., then poured into a slight excess of cold 10% aqueous sodium hydroxide. Benzene-extraction yielded a dark gum, which when recrystallised from ethanol afforded β-N-*benzanilidopropiophenone* (I; R = R′ = H, R″ = Bz, R‴ = Ph), needles, m. p. 132° (4 g., 65%) (Found: C, 80·1; H, 5·9; N, 4·5%; *M*, in boiling acetone, 362, 353. $C_{22}H_{19}O_2N$ requires C, 80·1; H, 5·8; N, 4·25%; *M*, 329). This ketone readily gave the *phenylhydrazone*, pale cream prisms, m. p. 166—167° (from ethanol) (Found: C, 79·9; H, 6·2; N, 10·0. $C_{28}H_{25}ON_3$ requires C, 80·2; H, 6·0; N, 10·0%). The 2 : 4-*dinitrophenylhydrazone* formed orange platelets, m. p. 205°, too insoluble for recrystallisation from the usual solvents (Found: N, 14·2. $C_{28}H_{23}O_5N_5$ requires N, 13·8%).

(*b*) In a modified experiment, the acid (2 g.) was converted into the acid chloride, which was then dissolved in chlorobenzene (15 c.c.); powdered aluminium chloride (2 g.) was added; the mixture was heated at 130—140° for 5 min. and then worked up. The syrupy residue from the benzene extract, when crystallised from a small quantity of warm ethanol, gave 2-N-*benzanilidoethyl* p-*chlorophenyl ketone* (I; R = R′ = H, R″ = Bz, R‴ = C_6H_4Cl), m. p. 113° (from ethanol) (1 g., 37%) (Found: C, 72·6; H, 5·35; N, 3·8. $C_{22}H_{18}O_2NCl$ requires C, 72·6; H, 5·0; N, 3·85%). The ketone gave a strong positive Beilstein test for halogen. It formed an insoluble 2 : 4-*dinitrophenylhydrazone*, orange platelets, m. p. 181° (Found: N, 12·9. $C_{28}H_{22}O_5N_5Cl$ requires N, 12·9%).

(*c*) The acid (2 g.) was converted into the chloride, which was treated in carbon disulphide (15 c.c.) with powdered aluminium chloride (2 g.); after 20 hr. at room temperature, the mixture was hydrolysed and extracted with benzene in the usual way. The residue when recrystallised from ethanol gave 1-benzoyl-1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline (II; R = R′ = H, R″ = Bz), m. p. 118° (lit.,[16] 122°) (0·4 g., 21%) (Found: C, 76·6; H, 5·5; N, 5·9. Calc. for $C_{16}H_{13}O_2N$: C, 76·5; H, 5·2; N, 5·6%). The oxoquinolone gave a scarlet 2 : 4-*dinitrophenylhydrazone*, m. p. 254—255° (insertion at 250°) (Found: N, 15·9. $C_{22}H_{17}O_5N_5$ requires N, 16·2%).

An authentic sample of the oxoquinoline (II; R = R′ = H, R″ = Bz), prepared by the benzoylation of 1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline, had m. p. and mixed m. p. 119—120°.

(iii) N-*Benzenesulphonyl*-β-*anilinopropionic acid.* (*a*) The acid chloride was prepared from the acid (I; R = R′ = H, R″ = SO_2Ph, R‴ = OH) (2 g.), and dissolved in benzene to which powdered aluminium chloride (2 g.) was added; the mixture was set aside at room temperature for 15 hr. Alkaline hydrolysis followed by benzene extraction ultimately afforded 1-*benzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydro*-4-*oxoquinoline*, m. p. 130° (from ethanol) (0·6 g., 32%) (Found: C, 63·0; H, 4·6; N, 4·9. $C_{15}H_{13}O_3NS$ requires C, 62·7; H, 4·6; N, 4·9%).

(*b*) The acid (4·8 g.) in benzene (25 c.c.) was heated under reflux for 30 min. with phosphorus pentachloride (3·2 g.); the mixture was then cooled to 0°, and stannic chloride (2·7 c.c.) in benzene (5 c.c.) was added. After 24 hr., the mixture was worked up and gave the above ketone (1·6 g., 35%), m. p. and mixed m. p. 130°. The 2 : 4-*dinitrophenylhydrazone* formed red-orange platelets, m. p. 218° (Found: N, 15·3. $C_{21}H_{17}O_6N_5S$ requires N, 15·0%).

The ketone (II; R = R′ = H, R″ = SO_2Ph) was hydrolysed to 1 : 2 : 3 : 4-tetrahydro-4-oxoquinoline in good yield by the method of Johnson *et al.*[2]

(iv) N-*Toluene*-p-*sulphonyl*-β-*anilinopropionic acid.* This acid afforded the 4-oxo-1-toluene-*p*-sulphonylquinoline (II; R = R′ = H, R″ = $SO_2{\cdot}C_6H_4Me$) by the following procedures.[1,2] The use of thionyl chloride in benzene, followed by aluminium chloride in the same solvent, gave yields from 35—50%, not consistently dependent upon the order of mixing of the cyclisation components or the nature (acid or alkaline) of the hydrolysis. A higher yield (*ca.* 70%) was achieved with the use of phosphorus pentachloride in benzene, followed by stannic chloride. Polyphosphoric acid (160°, 20 min.) was unsatisfactory, and gave only traces of an unidentified ketone.

The purified ketone had m. p. 141—142° (lit.,[1,2] 141—142°), pale cream crystals from ethanol (Found: N, 4·7. Calc. for $C_{16}H_{15}O_3NS$: N, 4·7%). It readily formed a highly crystalline *phenylhydrazone*, cream platelets, m. p. 232° (decomp.) (from dioxan) (Found: C, 67·8; H, 5·4; N, 10·8. $C_{22}H_{21}O_2N_3S$ requires C, 67·5; H, 5·4; N, 10·7%), and an orange 2 : 4-*dinitrophenylhydrazone*, m. p. 204—205° (Found: N, 14·7. $C_{22}H_{19}O_6N_5S$ requires N, 14·6%).

(v) N-*Benzenesulphonyl*-β-m-*methoxyphenylpropionic acid*. The acid (6·7 g.) was converted into the chloride by phosphorus pentachloride (4·2 g.) in benzene (40 c.c.), followed by stannic chloride (3·5 c.c.) at 0°; the mixture was set aside at room temperature for 15 hr., and when then worked up gave 1-*benzenesulphonyl*-1 : 2 : 3 : 4-*tetrahydro*-7-*methoxy*-4-*oxoquinoline* (IV), m. p. 138—139° (from ethanol) (3 g., 47%) (Found: C, 60·9; H, 5·05; N, 4·7. $C_{16}H_{15}O_4NS$ requires C, 60·6; H, 4·8; N, 4·4%). A lower yield (40%) was obtained by the thionyl chloride–aluminium chloride–benzene method. The mother-liquors were examined without success for the presence of the possible 5-methoxy-isomer. The ketone gave an insoluble deep orange 2 : 4-*dinitrophenylhydrazone*, m. p. 201° (Found: N, 14·2. $C_{22}H_{19}O_7N_5S$ requires N, 14·1%).

To obtain 1 : 2 : 3 : 4-tetrahydro-7-methoxy-4-oxoquinoline (II; R = R″ = H, R′ = OMe), a solution of the ketone (II; R = H, R′ = OMe, R″ = SO_2Ph) (2 g.) in acetic acid (2 c.c.), water (0·5 c.c.), and concentrated hydrochloric acid (2 c.c.) was boiled under reflux for 3 hr., then poured into water (25 c.c.) and extracted with ether. Evaporation of the extract gave a residue, which on fractional recrystallisation from ethanol yielded the unchanged ketone (0·2 g., 10%) and the required 4-oxoquinoline, m. p. 135—137°, depressed to 108—120° on admixture with unchanged ketone. The aqueous solution from the ether extraction was brought to pH 7 by the addition of powdered sodium carbonate, and a second ether-extraction gave a second crop of the 4-*oxoquinoline*; the combined crops (0·65 g., 63%), when recrystallised from ethanol, formed pale yellow prisms, m. p. 139° (Found: C, 66·6; H, 5·7; N, 8·1; OMe, 17·8. $C_{10}H_{11}O_2N$ requires C, 67·8; H, 6·2; N, 7·9; OMe, 17·5%). The pale yellow ethanolic solution has a blue fluorescence. The ketone gave a deep purple 2 : 4-*dinitrophenylhydrazone*, m. p. 274° (Found: N, 20·4. $C_{16}H_{15}O_5N_5$ requires N, 19·7%).

(vi) N-*Toluene*-p-*sulphonyl*-β-m-*methoxyphenylpropionic acid*. The acid (4 g.) was converted into its chloride by treatment with phosphorus pentachloride (2·6 g.) in benzene (25 c.c.) under reflux (30 min.), and cyclisation was effected with stannic chloride (2·1 c.c.) as before. The dark brown-yellow mixture, with a red oily lower layer, was poured into dilute aqueous sodium hydroxide and extracted with benzene. Evaporation of the extract afforded a dark brown syrup, which on fractional crystallisation from ethanol gave first 1 : 2 : 3 : 4-*tetrahydro*-7-*methoxy*-4-*oxo*-1-*toluene*-p-*sulphonylquinoline* (V) (0·75 g., 20%), m. p. 94—98°, increased to 104—105° by recrystallisation from ethanol (Found: C, 61·6; H, 5·5; N, 4·5. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·2; N, 4·25%). It gave a deep orange 2 : 4-*dinitrophenylhydrazone*, melting to a glass at 182—184°, then remelting at 212° (Found: N, 13·8. $C_{23}H_{21}O_7N_5S$ requires N, 13·7%).

The second ketonic fraction, from the ethanolic mother-liquors, furnished the 5-*methoxy*-isomer (VI) (0·75 g., 20%), m. p. 114° after recrystallisation from ethanol (Found: C, 61·9; H, 5·2; N, 4·5%). The 2 : 4-*dinitrophenylhydrazone* formed vermilion platelets, m. p. 202° (Found: N, 14·0%). A mixture of the isomeric ketones (V) and (VI) had m. p. 109—112°.

We are greatly indebted to Dr. N. Sheppard for valuable discussion of the infrared spectra.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, April 30th,* 1957.]

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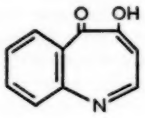
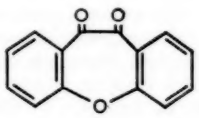
838. *Seven-membered Heterocyclic Systems. Part I. The Attempted Friedel–Crafts Cyclisation of γ-Arylsulphonamidobutyric Acids.*

By JOHN T. BRAUNHOLTZ and FREDERICK G. MANN.

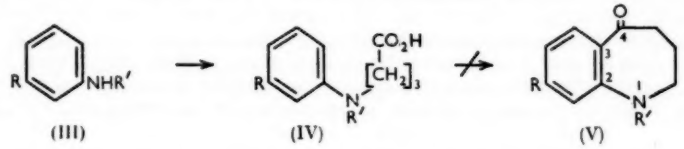
4 : 5 : 6 : 7-Tetrahydro-1-methyl-4-oxo-2 : 3-benzazepine (V; R = H, R′ = Me) has been prepared by a Dieckmann diester cyclisation. In this paper we describe attempts to establish an alternative synthesis of ketones of this type by Friedel–Crafts ring-closure of a variety of γ-arylsulphonamidobutyric acids; unexpected, and in certain cases rather complex, reactions occur with the formation of derivatives of *N*-phenylpyrrolid-2-one.

ALTHOUGH the synthesis and properties of non-benzenoid aromatic hydrocarbons and their derivatives have been widely studied in recent years, very few examples of analogous systems, such as the aza-azulenes,[1] in which one or more ·CH: groups are replaced by a heteroatom, have been reported. In particular, the azabenzotropolone (I) and its 7-ring isomers, are unknown, although two accounts of a synthesis of the related dibenzo-system containing oxygen (II) have recently appeared.[2,3]


(I)


(II)

In an initial study of compounds of type (I), we have attempted to prepare substituted 4 : 5 : 6 : 7-tetrahydro-4-oxo-2 : 3-benzazepines (V) by the sequence of reactions described below (in which R′ = SO_2Ph or $SO_2{\cdot}C_6H_4Me$, and R = H, Me, or OMe), as an alternative to the Dieckmann-type ring closure which Astill and Boekelheide [4] and we [5] have independently found to be effective in the preparation of the benzazepine (V; R = H, R′ = Me); the proposed conversion of the compound (V) into the azatropolone (I) would then be undertaken by a route analogous to that employed in the carbocyclic series by Cook *et al.*[6] The projected synthesis fails, however, at the cyclisation stage, the products of which are arylpyrrolid-2-ones, accompanied by arylsulphonyl chlorides or derivatives thereof.


(III) (IV) (V)

1-Bromo-3-cyanopropane [7] reacts readily, in aqueous ethanol containing one equivalent of sodium hydroxide, with the sulphonyl derivatives of aniline, *m*-toluidine and *m*-anisidine (III; R = H, Me or OMe, R′ = SO_2Ph or $SO_2{\cdot}C_6H_4Me$) and of β-naphthylamine, but does not do so with the benzoyl derivative of *m*-anisidine (III; R = OMe, R′ = Bz).

The 3-(substituted amino)-1-cyanopropanes thus obtained undergo smooth alkaline hydrolysis, without loss of the sulphonyl groups, to the stable crystalline acids (IV; R = H, Me, or OMe, R′ = SO_2Ph or $SO_2{\cdot}C_6H_4Me$) and their β-naphthyl analogues.

[1] Pauson, *Chem. Rev.*, 1955, **55**, 9.
[2] Mathys, Prelog, and Woodward, *Helv. Chim. Acta*, 1956, **39**, 1095.
[3] Rees, *Chem. and Ind.*, 1957, 76.
[4] Astill and Boekelheide, *J. Amer. Chem. Soc.*, 1955, **77**, 4079.
[5] Braunholtz and Mann, *Chem. and Ind.*, 1957, 266.
[6] Cook, Gibb, Raphael, and Somerville, *J.*, 1952, 603.
[7] Derick and Hess, *J. Amer. Chem. Soc.*, 1918, **40**, 537.

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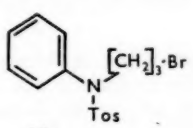
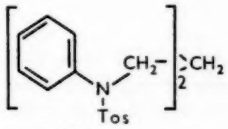
The corresponding **3-*m*-acetanisido-1-cyanopropane**, prepared by a different route, is deacetylated under these conditions and yields the acid (IV; R = OMe, R′ = H).

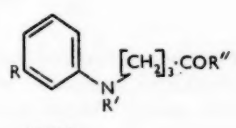
In an attempt to develop a better overall synthesis of the acids (IV), toluene-*p*-sulphonanilide (III; R = H, R′ = $SO_2{\cdot}C_6H_4Me$) was treated in alkaline solution with trimethylene dibromide; the 1 : 3-disubstituted propanes (VI) and (VII; Tos = *p*-$SO_2{\cdot}C_6H_4Me$) were obtained under a variety of conditions, but the yields of (VI) were too low to form the basis of an alternative route to the acids of type (IV). All attempts to prepare these acids by the reaction of amides (III; R = H, R′ = Bz, SO_2Ph, or $SO_2{\cdot}C_6H_4Me$) with γ-bromobutyric acid or its ethyl ester in the presence of aqueous-alcoholic alkali failed.



(VI)



(VII)



(VIII)

In view of the unusual results obtained in the cyclisation experiments described below, the ready conversion of the acids (IV; R = H or OMe, R′ = $SO_2{\cdot}C_6H_4Me$) into their acid chlorides has been demonstrated by identification of the latter as the *p*-toluidides (VIII; R = H or OMe, R′ = $SO_2{\cdot}C_6H_4Me$, R″ = $NH{\cdot}C_6H_4Me$), which were in each case obtained in high yield.

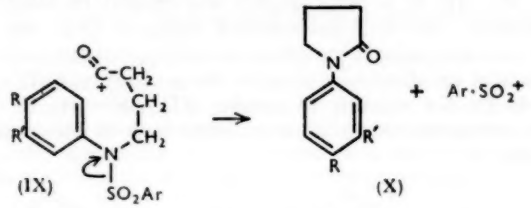
We have examined the Friedel–Crafts reactions of the chloride of the acid (IV; R = H, R′ = $SO_2{\cdot}C_6H_4Me$) under a variety of conditions as an introduction to the detailed investigation of the products obtained in attempted cyclisations of γ-arylaminobutyric acids (IV) containing an activated aromatic nucleus. Our results, obtained with the above acid chloride, agree in several respects with those briefly described by Astill and Boekelheide,[4] who in attempting its cyclisation in benzene isolated phenyl *p*-tolyl sulphone and 1-phenylpyrrolid-2-one in approximately equal yields.

We find that γ-(toluene-*p*-sulphonanilido)butyryl chloride, when treated with aluminium chloride in benzene at room temperature, ultimately affords phenyl *p*-tolyl sulphone in *ca.* 50% yield. The remainder of the reaction product affords in very small yield the phenyl ketone (VIII; R = H, R′ = $SO_2{\cdot}C_6H_4Me$, R″ = Ph) arising from the interaction of the chloride with the solvent. The ability of the chloride of the acid (IV; R = H, R′ = $SO_2{\cdot}C_6H_4Me$) to form open-chain ketones is shown by its similar reaction with anisole, to give the ketone (VIII; R = H, R′ = $SO_2{\cdot}C_6H_4Me$, R″ = $C_6H_4{\cdot}OMe$) in *ca.* 15% yield. If a less reactive solvent (*e.g.*, carbon disulphide) or a less powerful catalyst (*e.g.*, stannic chloride) is used, toluene-*p*-sulphonyl chloride is isolated in rather low yield from the original reaction product.

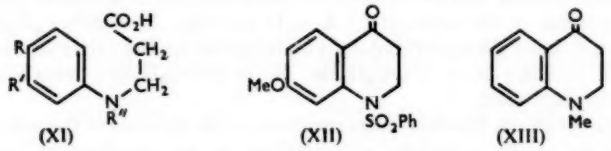
The ready cyclisation at room temperature of a wide variety of β-sulphonamidopropionic acids (XI) (see preceding paper) [8] shows that the sulphonamido-group is not inherently unstable under the above conditions, but that some other feature of the butyric acid (IV; R = H, R′ = $SO_2{\cdot}C_6H_4Me$) is responsible for the unexpected course of the reaction. It is probable that a process represented as (IX ⟶ X), in which the carbonium ion attacks the nitrogen, with the expulsion of a sulphonyl ion, is favoured by the consequent formation of the stable pyrrolid-2-one ring rather than the desired seven-membered system. It is, however, noteworthy that phenyl *p*-tolyl sulphone has also been recorded by Johnson *et al.*[9] as a by-product from the cyclisation of the acid (XI; R = H, R′ = Cl, R″ = $SO_2{\cdot}C_6H_4Me$) at room temperature; the other product isolated was the desired **7-chloro-1 : 2 : 3 : 4-tetrahydro-1-toluene-*p*-sulphonyl-4-oxoquinoline**. It is unlikely in this case that a four-membered lactam analogous to (X) was formed. We

[8] Braunholtz and Mann, *J.*, 1957, preceding paper.
[9] Johnson, Woroch, and Buell, *J. Amer. Chem. Soc.*, 1949, **71**, 1901.

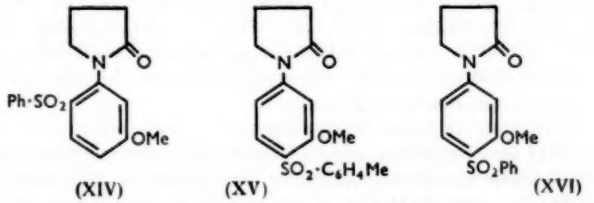
have now found that 1-benzenesulphonyl-1 : 2 : 3 : 4-tetrahydro-7-methoxy-4-oxoquinoline (XII) reacts with aluminium chloride in boiling benzene to give diphenyl sulphone in good yield, no other product being identified.



It was hoped that the desired cyclisation (IV ⟶ V) would be promoted, at the expense of pyrrolidone formation, by the use of substituted butyric acids containing activated aromatic nuclei. When, however, the acid (IV; R = Me, R′ = SO_2Ph), or the analogous compound derived from β-naphthylamine, was treated in benzene at room temperature with thionyl chloride followed by aluminium chloride, intractable tars were obtained.



The Friedel–Crafts treatment (in benzene at room temperature), when applied to the *m*-anisidine derivatives (IV; R = OMe, R′ = SO_2Ph and $SO_2{\cdot}C_6H_4Me$), gave as the most readily isolated and purified products (yields *ca.* 12%) two closely similar crystalline compounds, [A], $C_{17}H_{17}O_4NS$, m. p. 200°, and [B], $C_{18}H_{19}O_4NS$, m. p. 222°, respectively. These substances have been isolated repeatedly and under the wide range of conditions summarised in Table 2 (p. 4181). In certain cases the use of benzene as solvent led to the isolation of diphenyl or phenyl *p*-tolyl sulphone; alumina chromatography of a benzene solution of the reaction product from a cyclisation in chlorobenzene, after separation of compound [A], gave 1-*m*-methoxyphenylpyrrolid-2-one (X; R = H, R′ = OMe) in *ca.* 30% yield.



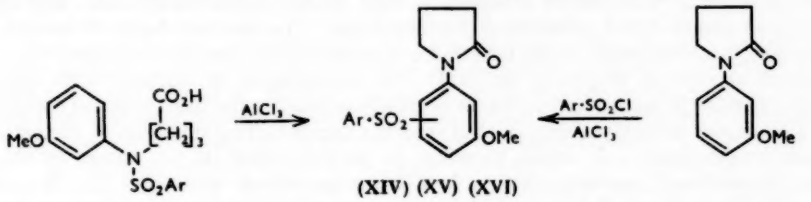
The following evidence shows that compounds [A] and [B] are 1-(2-benzenesulphonyl-5-methoxyphenyl)pyrrolid-2-one (XIV) and 1-(3-methoxy-4-toluene-*p*-sulphonylphenyl)-pyrrolid-2-one (XV) respectively; the migration of the arylsulphonyl group to the aromatic nucleus is a notable feature of these compounds, which are isomeric with the expected ketones.

(*a*) Synthetic experiments, suggested by the properties of (XIV) and (XV) summarised below (*b* and *c*), provide conclusive evidence for the structures assigned to these compounds.

When 1-*m*-methoxypyrrolid-2-one (X; R = H, R′ = OMe) is treated (in benzene at room temperature) with toluene-*p*-sulphonyl chloride in the presence of aluminium chloride, a moderate yield is obtained of a compound identical with (XV). When benzenesulphonyl

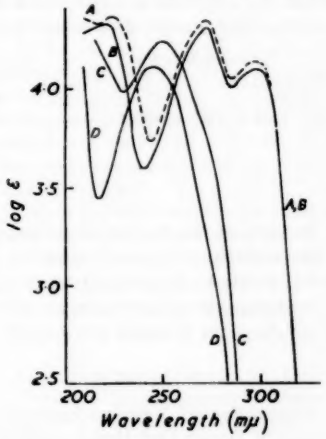
chloride is similarly used, a new compound, $C_{17}H_{17}O_4NS$, m. p. 223°, is obtained; this is isomeric with (XIV), which it closely resembles, and is assigned the structure (XVI) analogous to that of the toluene-*p*-sulphonyl compound. The two paths leading to substances (XIV), (XV), and (XVI) may therefore be summarised in the annexed scheme.

The positional assignment of the arylsulphonyl group in the compounds (XIV), (XV), and (XVI) involves a distinction between three possible isomers; one of these, in which this group is in the *ortho*-position to both methoxyl and nitrogen, is unlikely on steric grounds. The infrared spectra of the three compounds confirm, however, that the aromatic substitution is of the 1 : 2 : 4-type; this is characterised by strong absorption bands at 835 cm.$^{-1}$ (XIV), 840 cm.$^{-1}$ (XV), and 837 cm.$^{-1}$ (XVI), distinct in the case of (XV) from another strong band, at 814 cm.$^{-1}$, assigned to the $SO_2{\cdot}C_6H_4Me$ radical.



(XIV) (XV) (XVI)

There is a striking similarity (see Figure) between the ultraviolet spectra of 1-phenylpyrrolid-2-one and that of the Friedel–Crafts product derived from (IV; R = OMe, R′ = SO_2Ph); on the other hand, the sole product obtainable in the toluene-*p*-sulphonyl



Ultraviolet absorption spectra of ethanolic solutions of:
(*A*) 1-(3-*Methoxy*-4-*toluene*-p-*sulphonyl*)- (XV),
(*B*) 1-(4-*Benzenesulphonyl*-3-*methoxy*)- (XVI), *and*
(*C*) 1-(2-*Benzenesulphonyl*-5-*methoxy*)-*phenylpyrrolid*-2-*one* (XIV), *and*
(*D*) 1-*Phenylpyrrolid*-2-*one*.

series is related very closely spectroscopically (and presumably structurally) to that obtained from the reaction between 1-*m*-methoxyphenylpyrrolid-2-one and benzenesulphonyl chloride. This confirms the structures (XV) and (XVI) assigned to the latter pyrrolid-2-ones, the spectra of which are of the more complex type, with long wavelength absorption in the 300 mμ region; steric hindrance to coplanarity in the compound (XIV) is reflected in its ultraviolet spectrum, which is of a simple type and has no absorption maximum beyond 250 mμ.

The detailed course of the reactions whereby the acids (IV; R = OMe, R′ = SO_2Ph and $SO_2{\cdot}C_6H_4Me$) give rise to the pyrrolidones (XIV) and (XV) respectively is not certain, nor is it known why these two compounds are of different types. It would, however, be expected that both the direct sulphonylation reactions of 1-*m*-methoxyphenylpyrrolid-2-one lead to substitution in the least hindered position of the aromatic nucleus.

XUM

Confirmatory evidence, obtained in the initial studies of (XIV) and (XV), may be summarised as follows:

(*b*) The two Friedel–Crafts products do not react with hydrazine or 2 : 4-dinitrophenylhydrazine, and the arylsulphonyl group is not removed by vigorous treatment with acid. We found however that the oxoquinolines, *e.g.*, (XII), of structure analogous to (V), behave normally in both respects; furthermore, 4 : 5 : 6 : 7-tetrahydro-1-methyl-4-oxo-2 : 3-benzazepine (V; R = H, R′ = Me), in which interaction between the amine and the carbonyl groups (with consequent reduction of ketonic properties) would be greater than in (V; R = OMe, R′ = SO_2Ar), has recently been shown also to possess ketonic properties.[5]

(*c*) Infrared evidence confirms the presence of the carbonyl group in the two products; the positions of the absorption maxima (1699 and 1703 cm.$^{-1}$) are compared in Table 1 with those of several related compounds, both cyclic amino-ketones (six- and seven-membered rings) and 1-substituted pyrrolid-2-ones. In the tetrahydro-4-oxoquinoline series (see preceding paper [8]) the 1-methyl compound (XIII) has approximately the same carbonyl absorption frequency as (XII); the conjugation of nitrogen with carbonyl which exists in the former amino-ketone is greatly reduced in the sulphonylated compound, but the nuclear methoxyl group in (XII) exerts a compensating influence on the carbonyl absorption frequency. It would, therefore, be predicted that the ν_{CO} values for the two new "cyclisation" products, if they had the amino-ketone structures (V; R = OMe, R′ = SO_2Ph or $SO_2{\cdot}C_6H_4Me$), would be approximately equal to that observed for (V; R = H, R′ = Me), *i.e.*, 1665 cm.$^{-1}$. On the other hand, the observed frequencies are compatible with the allotted pyrrolid-2-one structures (XIV) and (XV).

TABLE 1. *Infrared absorption, in the region* 1650—1710 *cm.*$^{-1}$, *of cyclic amino-ketones and* 1-*arylpyrrolid-2-ones, determined with solid samples in Nujol mull* (*unless otherwise stated*).

Amino-ketones	ν_{CO} (cm.$^{-1}$)	Pyrrolid-2-ones	ν_{CO} (cm.$^{-1}$)
(XII)	1675	(XIV)	1699
(XIII)	1677	(XV)	1703
(V; R = H, R′ = Me) *	1665	(XVI)	1700
		(X; R = R′ = H)	1672
		(X; R = Me, R′ = H)	1683
		(X; R = H, R′ = OMe)	1683

* Liquid film.

In view of the results discussed above, the attempted direct Friedel–Crafts cyclisations of the substituted γ-arylaminobutyric acids (IV) have been abandoned. Their success would clearly be dependent on the use of an acyl group R′ in (IV) which is not susceptible to displacement in the reaction of the acid chloride with aluminium chloride. The successful synthesis of ketones of type (V) by other routes will be described later.

EXPERIMENTAL

Preparation of 1-*Bromo*-3-*cyanopropane*.—1-Bromo-3-cyanopropane was prepared by the method of Derick and Hess,[7] modified only in the use of commercial methanol without additional drying; the bromo-cyanide, b. p. 91—94°/14 mm., was obtained in 28% yield.

The benzenesulphonyl and toluene-*p*-sulphonyl derivatives of the appropriate arylamines were prepared by the usual Schotten–Baumann method. N-*Benzoyl*-m-*anisidine* was obtained as colourless crystals, m. p. 111° from ethanol (Found: N, 6·3. $C_{14}H_{13}O_2N$ requires N, 6·15%): Grammaticakis [10] gives m. p. 112° without analytical figures.

Reaction of Toluene-p-*sulphonanilide with* 1 : 3-*Dibromopropane*.—The sulphonanilide (5 g.) in ethanol (15 c.c.)–water (5 c.c.) containing sodium hydroxide (0·8 g.) was added to 1 : 3-dibromopropane (4 g.) in hot ethanol (10 c.c.). The mixture was heated under reflux for 3 hr., then diluted with water (50 c.c.). The precipitated heavy oil on fractional crystallisation from methanol ultimately gave the less soluble 1 : 3-*di*(*toluene*-p-*sulphonanilido*)*propane* (VII) (2·5 g., 46%), m. p. 135° (Found: C, 65·3; H, 5·8; N, 5·45. $C_{29}H_{30}O_4N_2S_2$ requires C, 65·3; H, 5·65; N, 5·3%) and the more soluble 1-*bromo*-3-(*toluene*-p-*sulphonanilido*)*propane* (VI) (1 g.,

[10] Grammaticakis, *Bull. Soc. chim. France*, 1951, 220.

14%), m. p. 66° after recrystallisation from aqueous methanol (Found: C, 52·5; H, 5·0; N, 3·85. $C_{16}H_{18}O_3NSBr$ requires C, 52·2; H, 4·95; N, 3·8%). The latter compound gave a strongly positive Beilstein test. Variation of the reaction conditions did not increase the yield of (VI).

Preparation of γ-Arylaminobutyric Acids.—(i) *γ-Benzenesulphonanilidobutyric acid* (IV; R = H, R′ = SO_2Ph). A solution of benzenesulphonanilide (4·6 g.) and 1-bromo-3-cyanopropane in ethanol (15 c.c.)–water (3 c.c.) containing sodium hydroxide (1 g.) was heated under reflux for 4½ hr. It was then concentrated and diluted with water (25 c.c.), depositing the crystalline 1-(*benzenesulphonanilido*)-3-*cyanopropane*, m. p. 81° from aqueous ethanol (5·5 g., 93%) (Found: C, 63·6; H, 5·35; N, 9·35. $C_{16}H_{16}O_2N_2S$ requires C, 63·9; H, 5·1; N, 9·5%).

The nitrile was readily hydrolysed when heated under reflux (4½ hr.) in ethanol (20 c.c.)–water (6 c.c.) containing potassium hydroxide (6 g.). When the mixture was acidified with concentrated hydrochloric acid, a heavy oil separated and soon solidified. Recrystallisation from aqueous ethanol gave the *acid* (IV; R = H, R′ = SO_2Ph), m. p. 104° (5 g., 86%) (Found: C, 60·7; H, 5·25; N, 4·55. $C_{16}H_{17}O_4NS$ requires C, 60·3; H, 5·35; N, 4·4%).

(ii) *Other (closely related) γ-butyronitriles and γ-butyric acids.* The following nitriles and acids were similarly prepared; 1-*cyano*-3-(*toluene*-p-*sulphonanilido*)*propane*, m. p. 102—104° from ethanol (Found: C, 64·5; H, 5·65; N, 8·9. $C_{17}H_{18}O_2N_2S$ requires C, 64·9; H, 5·75; N, 8·9%); 1-(*N*-benzenesulphonyl-*m*-toluidino)-3-cyanopropane, an oil; 1-*cyano*-3-(*N*-*toluene*-p-*sulphonyl*-m-*toluidino*)*propane*, m. p. 80° from aqueous ethanol (Found: C, 65·4; H, 5·9; N, 8·55. $C_{18}H_{20}O_2N_2S$ requires C, 65·7; H, 6·15; N, 8·55%): 1-(*N*-benzenesulphonyl-*m*-anisidino)-3-cyanopropane, an oil; 1-*cyano*-3-(*N*-*toluene*-p-*sulphonyl*-m-*anisidino*)*propane*, m. p. 93° from ethanol (Found: C, 62·8; H, 6·1; N, 8·4. $C_{18}H_{20}O_3N_2S$ requires C, 62·8; H, 6·0; N, 8·15%); 1-(*N*-benzenesulphonyl-β-naphthylamino)-3-cyanopropane and its *N*-toluene-*p*-sulphonyl-analogue, viscous syrups. *m*-Benzanisidide did not react with 1-bromo-3-cyanopropane under the conditions described above.

Hydrolysis of the nitriles by potassium hydroxide in aqueous ethanol under reflux gave the following *butyric acids*: γ-(Toluène-*p*-sulphonanilido)- (IV; R = H, R′ = $SO_2{\cdot}C_6H_4Me$), m. p. 164—165° from aqueous ethanol (lit.,[4] 165°) (Found: C, 61·3; H, 6·0; N, 4·5. Calc. for $C_{17}H_{19}O_4NS$: C, 61·3; H, 5·75; N, 4·2%): γ-(*N*-*benzenesulphonyl*-m-*toluidino*)- (IV; R = Me, R′ = SO_2Ph), m. p. 134° from aqueous ethanol (Found: C, 61·3; H, 5·4; N, 4·3. $C_{17}H_{19}O_4NS$ requires C, 61·3; H, 5·75; N, 4·2%); γ-(*N*-*toluene*-p-*sulphonyl*-m-*toluidino*)- (IV; R = Me, R′ = $SO_2{\cdot}C_6H_4Me$), m. p. 115° from aqueous ethanol (Found: C, 61·9; H, 5·9; N, 4·15. $C_{18}H_{21}O_4NS$ requires C, 62·2; H, 6·1; N, 4·05); γ-(*N*-*benzenesulphonyl*-m-*anisidino*)- (IV; R = OMe, R′ = SO_2Ph), m. p. 112° from benzene (Found: C, 58·6; H, 5·7; N, 4·0. $C_{17}H_{19}O_5NS$ requires C, 58·5; H, 5·5; N, 4·0%); γ-(*N*-*toluene*-p-*sulphonyl*-m-*anisidino*)- (IV; R = OMe, R′ = $SO_2{\cdot}C_6H_4Me$), m. p. 86—87° (from benzene–*cyclo*hexane) (Found: C, 59·9; H, 5·8; N, 3·9. $C_{18}H_{21}O_5NS$ requires C, 59·5; H, 5·8; N, 3·85%); γ-(*N*-*benzenesulphonyl*-β-*naphthylamino*)-, m. p. 175° from ethanol (Found: C, 64·8; H, 4·85; N, 4·0. $C_{20}H_{19}O_4NS$ requires C, 65·0; H, 5·2; N, 3·8); γ-(*N*-*toluene*-p-*sulphonyl*-β-*naphthylamino*)-, m. p. 142° from aqueous ethanol followed by benzene (Found: C, 65·5; H, 5·7; N, 3·95. $C_{21}H_{21}O_4NS$ requires C, 65·7; H, 5·5; N, 3·65%).

(iii) *Use of γ-bromobutyric ester.* A number of unsuccessful attempts were made (cf. Clemo and Perkin,[11] Elderfield *et al.*[12]) to bring about reaction between toluene-*p*-sulphonanilide or benzo-*m*-anisidide and ethyl γ-bromobutyrate in aqueous ethanol containing sodium hydroxide (either 2 mols. or a large excess). Unchanged amino-derivatives were recovered.

(iv) *Derivatives of acetyl*-m-*anisidine* (III; R = OMe, R′ = Ac). Acetyl-*m*-anisidine (16·5 g.) in xylene (75 c.c.) was heated at 130° with sodium wire (2·9 g.) for 1 hr.; hydrogen was evolved and a spongy white mass of the sodium derivative of acetyl-*m*-anisidine was formed. 1-Bromo-3-cyanopropane (20 g.) was added, and after a further 3 hours' heating the sodium bromide was filtered off and washed with ether, which was added to the xylene. Removal of the solvents left the impure 1-(acetyl-*m*-anisidino)-3-cyanopropane as a brown oil which partially decomposed on attempted distillation.

The nitrile could not be cyclised by the aluminium chloride–potassium chloride–sodium chloride melt method,[13] from which the starting material was not recovered.

[11] Clemo and Perkin, *J.*, 1924, **125**, 1608.
[12] Elderfield, Gensler, Bembry, Kremer, Brody, Hageman, and Head, *J. Amer. Chem. Soc.*, 1946, **68**, 1259.
[13] Allison, Braunholtz, and Mann, *J.*, 1954, 403.

XUM

Alkaline hydrolysis of the nitrile (3 g.) in boiling aqueous ethanol (10 c.c./20 c.c.) containing potassium hydroxide (5 g.) gave after 8 hr. crude γ-*m*-anisidinobutyric acid (IV; R = OMe, R′ = H) as a brown oil which was characterised by conversion into γ-(*N*-benzenesulphonyl-*m*-anisidino)butyric acid, m. p. 112°.

Characterisation of Acid Chlorides.—In view of anomalous results obtained in cyclisation reactions (below), simple derivatives of certain acid chlorides were prepared.

(i) γ-(*N*-Toluene-*p*-sulphonanilido)butyric acid (IV; R = H, R′ = SO_2·C_6H_4Me). The acid (0·5 g.) was converted by thionyl chloride in benzene into the syrupy acid chloride. *p*-Toluidine (0·35 g., 2 mols.) in dry benzene was added to the chloride (also in benzene), giving an immediate precipitate of the amine hydrochloride. The benzene layer when washed with water, dilute hydrochloric acid, and again with water, afforded the colourless γ-(*N-toluene*-p-*sulphonanilido*)*butyro*-p-*toluidide* (VIII; R = H, R′ = SO_2·C_6H_4Me, R″ = NH·C_6H_4Me) (0·55 g., 84%), m. p. 124° from benzene (Found: C, 68·5; H, 6·1; N, 6·85. $C_{24}H_{26}O_3N_2S$ requires C, 68·2; H, 6·2; N, 6·65%). Mixed m. p.s: with toluene-*p*-sulphonyl-*p*-toluidine, m. p. 95—110°; with phenyl *p*-tolyl sulphone, m. p. 95—120°.

(ii) γ-(*N*-Toluene-*p*-sulphonyl-*m*-anisidino)butyric acid (IV; R = OMe, R′ = SO_2·C_6H_4Me). The acid (0·5 g.) when treated as above gave *p*-toluidine hydrochloride (almost theoretical yield) and a syrup which eventually solidified and when recrystallised from benzene–*cyclo*hexane gave γ-(N-*toluene*-p-*sulphonyl*-m-*anisidino*)*butyro*-p-*toluidide* (VIII; R = OMe, R′ = SO_2·C_6H_4Me, R″ = NH·C_6H_4Me), m. p. 114—115° (Found: C, 66·3; H, 5·9; N, 6·5. $C_{25}H_{28}O_4N_2S$ requires C, 66·3; H, 6·2; N, 6·2%).

Preparation of 1-*Arylpyrrolid*-2-*ones.*—Authentic samples of three 1-arylpyrrolidones were prepared for comparative purposes: 1-Phenylpyrrolid-2-one (X; R = R′ = H) prepared by the action of polyphosphoric acid (100°, 1 hr.) on (IV; R = H, R′ = SO_2·C_6H_4Me) had m. p. 65—66° after crystallisation from ether–light petroleum (b. p. 40—60°) (Found: N, 8·7. Calc. for $C_{10}H_{11}ON$: N, 8·7%). Lit.,[4] m. p. 70—71°.

1-*p*-Tolylpyrrolid-2-one (X; R = Me, R′ = H) was obtained (43%) by the interaction of *p*-toluidine (10 g.) and γ-butyrolactone (10 g., 1·2 mols.) in a sealed vessel at 200° (12 hr.), the product crystallising when the reaction mixture was cooled. Recrystallisation from light petroleum (b. p. 60—80°) containing a few drops of ethanol gave the pyrrolid-2-one in needles, m. p. 87·5° (Found: C, 75·7; H, 7·65; N, 7·7. Calc. for $C_{11}H_{13}ON$: C, 75·4; H, 7·5; N, 8·0%). Lit.,[14] m. p. 88·5°. An attempt to prepare 1-*p*-nitrophenylpyrrolid-2-one in this way was unsuccessful, *p*-nitroaniline being the only crystalline material recovered.

A mixture of *m*-anisidine (15 g.) and γ-butyrolactone (13 g., 1·2 mols.) was heated at 220—230° under an air-condenser. After 3 hr. it was distilled, giving fractions (*a*) b. p. 85—110°/14 mm. (10 g.), mainly unchanged lactone, (*b*) b. p. 118—124°/14 mm. (11 g.), unchanged *m*-anisidine, and (*c*) b. p. 175—180°/3 mm. (2·5 g., 11%), which solidified and when recrystallised from ether–light petroleum (b. p. 40—60°) gave 1-m-*methoxyphenylpyrrolid*-2-*one* (X; R = H, R′ = OMe), m. p. 56° (Found: C, 69·0; H, 6·55; H, 7·45. $C_{11}H_{13}O_2N$ requires C, 69·1; H, 6·85; N, 7·35%).

Reaction of 1-m-*Methoxypyrrolid*-2-*one with Acyl Chlorides.*—(i) *With benzenesulphonyl chloride.* The pyrrolidone (0·5 g.) in dry chlorobenzene (10 c.c.) was heated at 130° for 5 min. with the sulphonyl chloride (0·5 g., 1·1 mols.) and powdered aluminium chloride (0·5 g., 1·5 mols.); the mixture was cooled, shaken with slight excess of dilute aqueous sodium hydroxide, and extracted with benzene. This extract on evaporation yielded colourless crystals which, recrystallised from ethanol–acetone, gave 1-(4-*benzenesulphonyl*-3-*methoxy*)*phenylpyrrolid*-2-*one* (XVI), m. p. 223° (0·1 g., 12%) (Found: C, 61·3; H, 5·5; N, 4·35. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·2; N, 4·25%), mixed m. p. with the Friedel–Crafts product from γ-(*N*-benzenesulphonyl-*m*-anisidino)butyric acid, 175—185°.

(ii) *With toluene*-p-*sulphonyl chloride.* The pyrrolidone (0·5 g.), treated as above, but with toluene-*p*-sulphonyl chloride, afforded 1-(3-methoxy-4-toluene-*p*-sulphonyl)phenylpyrrolid-2-one (0·1 g., 12%), m. p. 222° (from ethanol–acetone), identical with the pyrrolid-2-one obtained from the attempted cyclisation.

Attempted Cyclisation of the γ-Substituted Butyric Acids.—(i) γ-*Toluene*-p-*sulphonanilidobutyric acid* (see also Astill and Boekelheide [4]). The acid (5 g.) was converted in the usual way into the chloride, which was treated in benzene with powdered aluminium chloride (5 g.) and set aside for 20 hr. The mixture was poured into a slight excess of aqueous sodium hydroxide

[14] Tafel and Stern, *Ber.*, 1900, **33**, 2235.

and extracted with benzene, which on evaporation yielded a brown syrup, which was dissolved in warm ethanol. A crystalline product was obtained, and on further recrystallisation from ethanol yielded phenyl *p*-tolyl sulphone (1·7 g., 50%), m. p. 125° (Found: C, 67·2; H, 5·0. Calc. for $C_{13}H_{12}O_2S$: C, 67·3; H, 5·15%) (lit.,[15] m. p. 127—127·5°. The original ethanolic mother-liquors when treated with 2 : 4-dinitrophenylhydrazine furnished in very small yield *γ-toluene-p-sulphonanilidobutyrophenone* 2 : 4-*dinitrophenylhydrazone*, orange-red platelets, m. p. 200—202° (insertion at 195°), after crystallisation from aqueous dioxan (Found: C, 60·3; H, 4·45; N, 12·5. $C_{29}H_{27}O_6N_5S$ requires C, 60·7; H, 4·75; N, 12·2%).

Small yields (15—25%) of free toluene-*p*-sulphonyl chloride, identified by m. p. and mixed m. p., were isolated when stannic chloride was employed in place of aluminium chloride, or when carbon disulphide replaced benzene.

In another experiment, anisole (2 g.) was added to a cyclisation mixture derived from the acid (5 g.) as described above. The deep purple mixture was set aside for 15 hr. and then worked up. The residue from the benzene extract had an odour of anisole, and did not crystallise. It was therefore treated in ethanol with 2 : 4-dinitrophenylhydrazine, giving p-*methoxyphenyl* 3-N-*toluene*-p-*sulphonanilidopropyl ketone* 2 : 4-*dinitrophenylhydrazone*, m. p. 226—228° (from dioxan) (Found: C, 59·8; H, 5·1; N, 11·8. $C_{30}H_{29}O_7N_5S$ requires C, 59·7; H, 4·85; N, 11·6%): 0·5 g., 13%.

(ii) *γ*-(N-*Benzenesulphonyl*-m-*toluidino*)- *and* *γ*-(N-*benzenesulphonyl*-β-*naphthylamino*)-*butyric acid*. Conversion of these acids into their chlorides, followed by treatment with aluminium chloride, gave ultimately dark tars from which no crystalline product could be isolated, although benzenesulphonyl chloride was in each case identified by its odour.

(iii) *γ*-(N-*Benzenesulphonyl*-m-*anisidino*)*butyric acid*. Many attempts to cyclise this acid are summarised in Table 2. In addition to other products, 1-(2-*benzenesulphonyl*-5-*methoxyphenyl*)*pyrrolid*-2-*one* (XIV), m. p. 200°, colourless crystals from ethanol–acetone, was isolated in variable yield (usually 10—15%) (Found: C, 61·8; H, 5·0; N, 4·35%; *M*, in boiling acetone, 351. $C_{17}H_{17}O_4NS$ requires C, 61·6; H, 5·2; N, 4·25%; *M*, 332).

TABLE 2. *Summary of procedures giving the pyrrolid-2-one* (XIV) *from the acid* (IV; R = OMe, R′ = SO_2Ph).

Method	Temp.	Time (hr.)	Yield (%)
(*a*) $SOCl_2$–C_6H_6; $AlCl_3$–C_6H_6	Room	15—112	5—10
(*b*) $SOCl_2$–C_6H_6; $AlCl_3$–C_6H_6	Reflux	¼—4	7
(*c*) $SOCl_2$–C_6H_6; $AlCl_3$–PhCl	110—140°	5—10 (min.)	8—15
(*d*) $SOCl_2$–C_6H_6; $SnCl_4$–C_6H_6	Room	48	3
(*e*) $SOCl_2$–C_6H_6; $SnCl_4$–C_6H_6	50—60°	3	3
(*f*) PCl_5–C_6H_6; $AlCl_3$–C_6H_6	Room	36	10
(*g*) PCl_5–C_6H_6; $SnCl_4$–C_6H_6	Room	15—20	15
(*h*) H_2SO_4–H_3PO_4	165°	½	5
(*i*) Polyphosphoric acid	115°; 150—160°	2; ½	3

In a typical experiment [(*a*), Table 2], the acid (1 g.) was converted into the chloride with thionyl chloride (1 c.c.) in benzene, and volatile materials removed under reduced pressure. A cooled solution of the residual brown syrup in dry benzene (20 c.c.) was treated with powdered aluminium chloride (1 g.). The mixture effervesced and became dark; after 20 hr. at room temperature, it was extracted with a slight excess of cold 10% aqueous sodium hydroxide, and the benzene layer on evaporation left a dark brown gum. A warm ethanolic solution of this residue soon deposited the crystalline pyrrolid-2-one (XIV) (100 mg., 10%). No other crystalline products could be isolated from the ethanolic mother-liquors, which showed no ketonic properties but had the smell of benzenesulphonyl chloride.

This experiment, with the time of reaction extended to 40 hr., gave a slightly increased yield of (XIV), and when it was extended to 112 hr. a very small yield of ketonic material was also isolated from the ethanolic mother-liquors (as the 2 : 4-dinitrophenylhydrazone), having probably been formed by reaction of the acid chloride with benzene.

When a large-scale cyclisation (5 g. of acid in 40 c.c. of benzene) was attempted, the major crystalline product (*ca.* 50%) was diphenyl sulphone, m. p. 122—123° (lit.,[16] 124°) (Found: C, 66·6; H, 4·7. Calc. for $C_{10}H_{12}O_2S$: C, 66·1; H, 4·6%), separated with difficulty by fractional crystalline from the pyrrolidone (XIV).

[15] Beringer, Brierley, Drexler, Gindler, and Lumpkin, *J. Amer. Chem. Soc.*, 1953, **75**, 2711.
[16] Hinsberg, *Ber.*, 1910, **43**, 289.

XUM

Reactions in chlorobenzene [(*c*) Table 2] gave slightly improved yields of the pyrrolidone (XIV); a crystalline sulphone was not obtained, but chromatography (alumina) of a benzene extract of the products after removal of (XIV) gave 1-*m*-methoxyphenylpyrrolid-2-one (X; R = H, R′ = OMe) as the major eluate (benzene), followed (benzene–ethanol) by a small quantity of uncrystallisable black tar.

(iv) *γ-(Toluene-*p*-sulphonyl-*m*-anisidino)butyric acid.* Preparation of the acid chloride, and subsequent cyclisation attempts, were carried out under conditions corresponding to those in Table 2.

*1-(3-Methoxy-4-toluene-*p*-sulphonyl)phenylpyrrolid-2-one* (XV), m. p. 222° (from ethanol–acetone), was obtained in 5—10% yield (Found: C, 62·9; H, 5·45; N, 4·15. $C_{18}H_{19}O_4NS$ requires C, 62·6; H, 5·55; N, 4·05%). In a typical prolonged experiment (room temperature, 100 hr.) phenyl *p*-tolyl sulphone (30%) and the pyrrolidone (XV) (4%) were obtained.

Chemical Properties of the Pyrrolid-2-ones (XIV) *and* (XV).—(i) The pyrrolidones were soluble in warm concentrated hydrochloric acid; partial recrystallisation of the unchanged pyrrolidones occurred on cooling, followed by their complete separation on dilution with water. 70% Sulphuric acid (1 day at room temperature) or boiling acetic acid–hydrochloric acid [9] were also without effect; a solution of (XIV) in concentrated sulphuric acid slowly darkened and charred.

(ii) The pyrrolidones were partially soluble in a boiling 30% solution of potassium hydroxide in aqueous ethanol (1 : 1 v/v) but were precipitated unchanged when the solutions were cooled.

(iii) Attempted reductions by lithium aluminium hydride in boiling ether, or sodium in boiling ethanol or butan-1-ol, failed, possibly because of the insolubility of the pyrrolidones (XIV) and (XV).

We are greatly indebted to Dr. A. J. Tetlow, who investigated the preparation of acetyl-*m*-anisidine derivatives and also carried out preliminary experiments on the preparation and cyclisation of *γ*-(*N*-benzenesulphonyl-*m*-anisidino)butyric acid (IV; R = OMe, R′ = SO_2Ph).

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839. *Colour and Constitution. Part III.*† *The Effect of Methyl Substitution on the α- and β-Bands of the Ultraviolet Spectrum of Alternant Hydrocarbons.*

By DAVID PETERS.

The effect of the methyl group on the α- and β-bands of the ultraviolet spectrum of alternant hydrocarbons is discussed in terms of the Hückel L.C.A.O. molecular-orbital theory. Substantial progress is possible from a purely theoretical analysis but, in order to obtain results as general as those for the *p*-band, the inclusion of an empirical element is essential.

IN general, either three or four bands (α, *p*, β, and β_1 in Clar's nomenclature [1] ‡) are observed in the ultraviolet spectrum of the condensed, six-membered ring, benzenoid hydrocarbons. They are believed to be of the π–π^* type, and a molecular-orbital interpretation of these bands, due to Dewar and Longuet-Higgins,[2] will be followed here and is shown diagrammatically in Fig. 1.

It has been shown (Parts I and II) that the effects of the common substituents on the *p*-band of the ultraviolet spectrum of these hydrocarbons may be quantitatively interpreted in terms of this model, the simple Hückel L.C.A.O. molecular-orbital theory. The *p*-band is, however, only one of the three or four bands appearing in these spectra, and the

† Parts I and II, *J.*, 1957, 646, 1993.

‡ Clar's actual nomenclature is α, *p*, β, and β′ but as the prime is used elsewhere in this paper with a different significance, Clar's β′ is written β_1.

[1] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1941.

[2] Dewar and Longuet-Higgins, *Proc. Phys. Soc.*, 1954, *A*, **67**, 795.

next step is clearly to examine how far these methods are applicable to the other bands. It is now shown that, as with the α- and β-bands of the parent hydrocarbons, difficulties arising from first-order configurational interaction [2,3] prevent a complete formal treatment, but if the inclusion of an empirical element is allowed a complete discussion of the methyl substituent is possible.

FIG. 1.

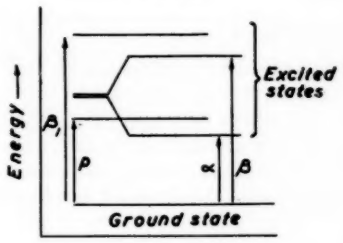
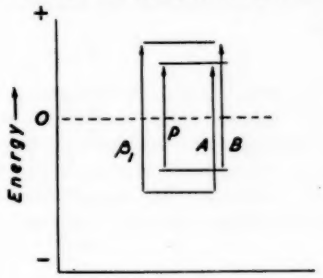


FIG. 2. *Hückel molecular orbitals.*



In the interpretation chosen, then, the *p*-band was derived in a simple manner from the highest bonding and lowest antibonding molecular orbitals, and the β_1-band similarly from the next highest and lowest molecular orbitals. The bathochromic effect of substituents on the *p*-band has been discussed: the bathochromic shifts ($\delta\lambda_{\beta_1}$) of the β_1-band are then given (in mμ) by the same expression as those of the *p*-band (Part I), *viz.*,

$$\delta\lambda_{\beta_1} = -123{\cdot}4c_{br}^2 \frac{1}{e_b(e_1^2 - e_b^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where e_b is the energy of the second-highest bonding molecular orbital of the hydrocarbon, c_{br} is the coefficient of this molecular orbital at the methylated carbon atom (r), and e_1 is the energy of the bonding molecular orbital of the methyl group. Since $e_b > e_a$, and the term $(e_1^2 - e_b^2)$ is relatively insensitive to small changes in e_b, the β_1-shifts will tend to be smaller than those of the *p*-band. For the smaller and more fully investigated benzenoid hydrocarbons, however, the β_1-band falls outside the range of the conventional spectrometers and there is little information by which the accuracy of equation (1) can be examined.

This simple derivation of the *p*- and β_1-bands does not carry over to the α- and β-bands. The latter are derived from the transitions marked *A* and *B* in Fig. 2 in the following way. The molecular orbitals of alternant hydrocarbons are symmetrically distributed about the arbitrary zero of energy (Fig. 2) and this symmetry leads to equal energy for transitions *A* and *B* (Fig. 1) and thus, within the approximations of the Hückel method, to a first-order configurational interaction between their excited states.[2,3] These excited states are then split by an interaction element γ:

$$\gamma = \sum_{i<j} \int \chi_A \frac{e^2}{r_{ij}} \chi_B \mathrm{d}t \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where χ_A and χ_B are the antisymmetrised wave functions of the excited states of the *A* and *B* transitions.

This completes the description of the origins of the π–π^* bands of the ultraviolet spectrum of the alternant hydrocarbons.

Method.—The effect of the methyl substituent is now examined by the method which proved of value for the *p*-band. As in the latter case, the inductive and mesomeric effects are discussed separately.[4]

[3] Moffitt, *J. Chem. Phys.*, 1954, **22**, 1820.
[4] Longuet-Higgins and Sowden, *J.*, 1952, 1404.

Inductive effect. This is defined as the effect arising from the change in coulomb integral ($\delta\alpha_r$) of the carbon atom (r) to which the substituent is attached. The well-known equation [5]

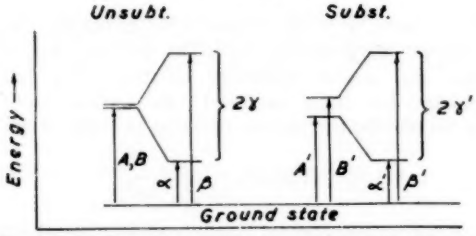
$$\delta\epsilon_i = c^2_{ir} \cdot \delta\alpha_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

(where $\delta\epsilon_i$ is the change in energy of the ith molecular orbital, c_{ir} is the atomic orbital coefficient of this orbital at the rth carbon atom) is applied to the A and B transitions with the result

$$\delta E_A = -\delta E_B = (c^2_{ar} - c^2_{br})\delta\alpha_r \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where δE_A and δE_B are the changes in the energy of the A and B transitions and c_{ar} and c_{br} are the atomic orbital coefficients at the rth carbon atom of the highest and second-highest bonding molecular orbitals respectively. The shifts δE_A and δE_B are equal in magnitude and opposite in sign, but, as c_{ar} and c_{br} are only accidentally equal, there is only trivial restriction on the magnitude of δE_A and δE_B. The resulting situation, shown diagrammatically in Fig. 3, is a symmetrical arrangement of the A and B levels about the

FIG. 3.†



† Throughout this paper, primes denote the substituted molecule.

original level of the A and B configurations. The sum of the A and B (and of the α and β) shifts is zero. The α' and β' levels are now separated by $2\gamma'$, where γ' is an interaction element analogous to γ.

At this point, further progress depends on an evaluation of γ and γ' or their difference, $\delta\gamma$. Unfortunately, it is not easy to evaluate these interaction elements quantitatively, nor does it seem possible to show that $\delta\gamma$ vanishes absolutely. We are faced with the same difficulties as those encountered when the α and β bands of the hydrocarbons themselves are examined by the molecular-orbital method.[2] If we are to confine ourselves to a purely theoretical treatment, we can only discuss the sum of the α- and β-shifts, since, although methods are available for the evaluation of the two electron integrals involved in γ,[6,7] they are rather too complex and uncertain for the present simple approach. If we are prepared to admit a purely empirical element into the discussion, further progress is possible. In Table 1 is gathered the available information on the shifts which result from the introduction of the purely inductive, ammonium ion group into alternant hydrocarbons.

When it is realised that these small shifts are the result of a substituent whose inductive power is many times greater than that of the methyl group,† it is clear that the inductive effect of the latter group on the ultraviolet spectrum is very small indeed. This conclusion constitutes a practical demonstration that, for the methyl group, $\delta\gamma$ is effectively zero. The expedient of introducing an empirical element into the discussion is unsatisfactory

† It has been estimated that the inductive effect of the ammonium ion is some ten times greater than that of the methyl group (Peters, *J.*, 1957, 2654).

[5] Coulson and Longuet-Higgins, *Proc. Roy. Soc.*, 1947, *A*, **191**, 39.
[6] Pariser and Parr, *J. Chem. Phys.*, 1953, **21**, 466.
[7] Pople, *Trans. Faraday Soc.*, 1953, **49**, 1375.

from a formal viewpoint but, if it is rejected, the even less attractive alternative of discussing the sum of the α- and β-shifts remains. The difficulty originates in a well-known shortcoming of the Hückel method.[3]

TABLE 1.

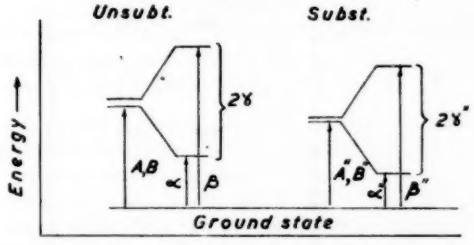
Hydrocarbon	Position of substituent	Shift *p*	Shift α	Shift β	Ref.
Naphthalene	2	0	0	+1	*a*
Anthracene	2	0—2	—	0	*b*
Phenanthrene	2	0	*	Small	*c*
	3	0	*	0	*c*
	9	0	*	Small	*c*
Pyrene	3	+5	+2	+2	*a*
1 : 2-Benzanthracene	3	+2—3	—	+2	*d*
	8	+6	+2	+2	*a*

* These α-band shifts are anomalous, there being a 20—30 mμ hypsochromic shift.

[a] Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127. [b] *Idem, Chem. Rev.*, 1947, **41**, 353. [c] Epsztein, *Mem. Services chim. État*, 1951, **36**, 245. [d] Jones, *J. Amer. Chem. Soc.*, 1941, **63**, 151.

Mesomeric effect. The model used for the conjugative action of the methyl group in the discussion of the *p*-band is applied to the α- and β-bands, the group being treated as a modified vinyl group with molecular orbitals of energy $\pm e_1$. The energy change (δe_i) of

FIG. 4.



the *i*th molecular orbital of energy e_i resulting from the formation of the bond of resonance integral β_{rs} from the carbon atom (r) of the ring to the carbon atom (s) of the methyl group is:[4,8]

$$\delta e_i = \sum_K \frac{c_{ir}^2 c_{ks}^2}{e_i - e_K} \beta_{rs}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where the c's are atomic orbital coefficients of nomenclature derived from the other quantities. The summation is over the two molecular orbitals of the methyl group ($K = \pm 1$). Applying equation (5) to the A and B transitions, we have

$$-\delta E_B = -\delta E_B = \left\{ \frac{e_a c_{ar}^2 \beta_{rs}^2}{e_a^2 - e_b^2} + \frac{e_b c_{br}^2 \beta_{rs}^2}{e_b^2 - e_1^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting the values of the universal constants and expressing the energy quantities in units of β, we have for the shifts $\delta\lambda_A$ and $\delta\lambda_B$ (in mμ)

$$\delta\lambda_A = \delta\lambda_B = \frac{247}{(e_a + e_b)^2} \left\{ \frac{e_b c_{br}^2}{e_b^2 - e_1^2} + \frac{e_a c_{ar}^2}{e_a^2 - e_1^2} \right\} \quad . \quad . \quad . \quad . \quad (7)$$

β_{rs} is taken as 0·51β (Part I), and a value of 30 kcal. per mole is used for β. Since $e_1 > e_a, e_b$, and e_a and e_b are negative energy quantities, it is clear that both the A and the B

[8] Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3341.

transitions are shifted bathochromically by the same amount. If $e_a = e_b$, then $c_{ar} = c_{br}$ and the expression reverts to that for the *p*-band. The situation before and after the introduction of the methyl group may be represented as in Fig. 4.

TABLE 2.

Hydrocarbon	Position of substituent	λ of parent (mμ) α	λ of parent (mμ) β	Shift (mμ) calc.	Shift (mμ) obs. α	Shift (mμ) obs. β	Ref.
Naphthalene	1	311	217	2	3	4	*a, b*
	2			4	8	4	*a, b*
Anthracene	1	—	252	5	—	1	*d*
	2			1	—	—	
	9			2	—	3—4	*c*
Phenanthrene	1	346	252	3	—	—	
	2			3	—	—	
	3			1	—	—	
	4			3	—	—	
	9			3	3	3—4	*b*
Chrysene	1	360	267	4	7	2	*e*
	2			2	2	2	*e*
	3			1	2	2	*e*
	4			5	1	2	*e*
	5			2	2	2	*e*
	6			2	6	4	*e*
Pyrene	1	372	272	1	2	2	*b*
	3			2	4	2	*f*
	4			4	3	3	*f*
3 : 4-Benzophenanthrene	1	354	281	3	5	3	*g*
	2			3	2	2	*g*
	5			2	8	5	*g*
	6			2	2	2	*g*
	7			1	1·5	1·5	*g*
	8			2	3	4	*g*
1 : 2-Benzanthracene	1′	384	287	4	3	0·5	*h*
	2′			2	3·5	3·5	*i*
	3′			2	1	1·5	*i*
	4′			4	3·5	5·5	*i*
	3			3	3·5	3·5	*i*
	4			2	0·5	1·5	*h*
	5			2	1·5	2	*h*
	6			2	0·5	1·5	*i*
	7			1	3	1	*i*
	8			2	2	3	*h*
	9			3	8·5	3·5	*h*
	10			3	5	4	*h*

[a] Morton and de Gouveia, *J.*, 1934, 916. [b] Friedel and Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951. [c] Ref. *b* of Table 1. [d] Mosby, *J. Org. Chem.*, 1953, **18**, 964. [e] Brode and Patterson, *J. Amer. Chem. Soc.*, 1941, **63**, 3252. [f] Förster and Wagner, *Z. phys. Chem.*, 1937, **37**, *B*, 352. [g] Badger and Walker, *J.*, 1954, 3238. [h] Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148. [i] Badger, Pearce, and Pettit, *J.*, 1952, 1112.

Having determined the behaviour of the *A* and *B* transitions, we must consider the derived α- and β-transitions. The situation is similar to that which arose when the inductive effect was examined, differing only in that the excited states of the *A* and the *B* transition are now of equal energy, but are bathochromically shifted. The interaction element γ'' differs from γ and we are again in the position of either retaining the purely theoretical approach and discussing only the sum of the α- and β-shifts or incorporating an empirical element and discussing the shifts separately. Adopting the latter course, we examine the data collected in Table 2 and find that again $\delta\gamma$ is zero to a reasonable approximation. Serious deviations from this generalisation are sometimes apparent in the positions where steric hindrance to coplanarity of the methyl group and the ring is known (Part I) to occur. As with the inductive effect, this appeal to experiment is not the most satisfactory solution but is the best available at present. It should be made clear that we cannot show on theoretical grounds alone that the α- and β-shifts are both bathochromic.

This situation is rather disappointing, for, experimentally, the α- and β-shifts seem to present no more complex a pattern than do those of the *p*-band. The experimental and calculated shifts are gathered in Table 2; e_1 is taken as 2·5β.

Discussion.—With regard to the experimental data, the β-band is usually an intense, well-developed single peak, sometimes with ill-defined shoulders or subsidiary peaks. The weak α-band is usually rather poorly developed, having an irregular fine structure, and difficulties sometimes arise in the estimation of the shift or in the identification of the vibrational peaks in the derivative. In anthracene and naphthacene, the α-band is completely hidden beneath the strong *p*-band.

One quite general conclusion from the experimental data collected in Table 2 is that, when positions subject to steric effects are excluded, the α- and β-shifts of all the monomethyl-substituted derivatives of any one of the parent molecules scatter less about their mean than is the case in the corresponding *p*-shifts. This may be seen from Table 3.

TABLE 3. *Range between minimum and maximum experimental shifts of monomethyl derivatives.*

Me deriv. of:	*p*	α	β	Me deriv. of:	*p*	α	β
Naphthalene	6	5	0	Pyrene	6	2	1
Anthracene	9	—	2—3	3 : 4-Benzanthracene	2	3	2
Chrysene	3	1	2	1 : 2-Benzanthracene	13·5	5	5

This close grouping of the α- and β-shifts is a consequence of equation (7), as the following argument shows. Consider a position in a given hydrocarbon at which $\delta\lambda_p$ is large. For this to be so, it is sufficient that c_{ar} be large; for $\delta\lambda_\alpha$ and $\delta\lambda_\beta$ to be large, however, both c_{ar} and c_{br} must be large at the same atom. Clearly, the latter situation is much less probable than that c_{ar} or c_{br} alone is large, and, in fact, the two atomic orbital coefficients tend to balance each other owing to the relation $2\sum_a c_{ar}^2 = 1$ (ref. 9). The same reasoning shows that a zero shift of the α- and β-bands is equally unlikely. This levelling of the α- and β-shifts is brought out quite clearly by the experimental data and has the practical result that the *p*-band is of greater value for diagnostic work.

For present purposes, the close grouping of the α- and β-shifts, together with the inaccuracies in the assumption that the α- and β-shifts are equal, make it difficult to compare the calculated and experimental shifts critically. On occasion, the range covered by these shifts is comparable with the probable error in the method. Since we now have three bands to discuss, however, conclusions of a broader kind are possible.

The methylnaphthalenes are well documented. De Laszlo [10] has commented that the *p*-band shows the larger bathochromic shift when the methylation is in the 1-position, while the α-band is affected to a greater extent by methylation in the 2-position. The results presented in Part I and in this paper explain this situation precisely.

In anthracene, *meso*-methylation causes a marked bathochromic shift of the *p*-band but a much smaller shift in the β-band. This qualitative conclusion is correctly predicted by the calculation, but there is some discrepancy between the magnitudes of the calculated and experimental shifts.

In phenanthrene, only the 9-methyl compound has a recorded spectrum. The agreement between the calculated and the observed values of the α- and β-shifts is good, and it may be predicted that the other positions will show quite small α- and β-shifts. This consideration alone will probably prove to be inadequate for the 4-position, steric hindrance to coplanarity of the methyl group and the ring causing a further, perhaps quite large, bathochromic shift.

Steric bathochromic shifts of the α- and β-bands are apparent in the 1- and the 6-position in chrysene. This is also the case with the *p*-band. These steric shifts are large compared with the mesomeric shifts, and are not equal for the α- and β-bands. In pyrene,

[9] Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193.
[10] De Laszlo, *Compt. rend.*, 1925, **180**, 203; *Proc. Roy. Soc.*, 1926, *A*, **111**, 377.

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the α- and β-shifts show the usual close grouping but it may be noticed that the zero shift of the *p*-band in the 4-position—owing to a zero value of the atomic orbital coefficient of the top bonding molecular orbital—does not occur in the α- and β-bands.

The most prominent feature of the α- and β-shifts of 3 : 4-benzophenanthrene is the marked steric bathochromic shift in the 5-position. The 9-position of 1 : 2-benzanthracene shows the same effect; in this hydrocarbon, the close grouping of the α- and β-shifts compared with the wide range of the *p*-shifts, is brought out very clearly.

This paper and Part I deal explicitly only with the methyl substituent, but there is no doubt that the larger alkyl groups behave similarly. Anderson and Smith's data [11] on the alkylnaphthalenes exemplify this generalisation. There is a possible complication in that the steric requirements of the larger alkyl groups may affect the magnitude of the steric bathochromic shifts which occur in certain positions with the methyl group, and also may cause such shifts in positions where the methyl group is not sufficiently bulky to do so. For this reason, caution is required in applying the present method to very bulky alkyl groups, such as the *tert.*-butyl radical.

Application of this method to simple olefins and polyenes is straightforward, as the success of Woodward's rules [12] shows. The latter are a particular case of this method.

The author is indebted to a Referee for several valuable suggestions.

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[11] Anderson and Smith, *J. Inst. Petroleum*, 1952, **38**, 426.
[12] Woodward, *J. Amer. Chem. Soc.*, 1941, **63**, 1123; 1942, **64**, 72, 76.

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840. *The Constitution of Barley Husk Hemicellulose.*

By G. O. Aspinall and R. J. Ferrier.

Barley husk hemicellulose, containing a small proportion (*ca.* 4%) of glucuronic acid residues, gave on hydrolysis xylose and arabinose in the ratio of 6 : 1. 2-*O*-D-Xylopyranosyl-L-arabinose was identified amongst the products of mild acid hydrolysis. Hydrolysis of the methylated polysaccharide afforded 2 : 3 : 5-tri-*O*-methyl-L-arabinose, 3 : 5-di-*O*-methyl-L-arabinose, 2 : 3 : 4-tri-*O*-methyl-D-xylose, 2 : 3-di-*O*-methyl-D-xylose, 2-*O*-methyl-D-xylose, and 3-*O*-methyl-2-*O*-(2 : 3 : 4-tri-*O*-methylglucuronosyl)-xylose in the approximate molar ratio 1 : 1 : 2 : 14 : 3 : 1. It is concluded from these and other experiments that the polysaccharide is composed of chains of 1 : 4-linked β-D-xylopyranose residues to which are attached side-chains of L-arabofuranose and 2-*O*-D-xylopyranosyl-L-arabofuranose residues through position 3, and glucopyranuronic acid residues through position 2. A small degree of branching in the backbone of D-xylose residues is indicated.

Most lignified tissues contain polysaccharides composed mainly of D-xylose residues. The xylans from various land plants, so far examined, are similar in possessing backbones of 1 : 4-linked β-D-xylopyranose units, but differ in the nature and number of sugar units attached as side-chains.[1] In continuation of structural investigations of the polysaccharide components of barley carried out in these laboratories [2] we have now examined the hemicellulose of barley husk.

Barley husks, separated from the grain, were extracted with benzene–ethanol to remove

[1] Hirst, *J.*, 1955, 2974; Aspinall and Schwarz, *Ann. Reports*, 1955, **52**, 261.
[2] Percival and McWilliam, *J.*, 1951, 2259; Aspinall and Telfer, *J.*, 1954, 3519; Aspinall, Hirst, and McArthur, *J.*, 1955, 3075.

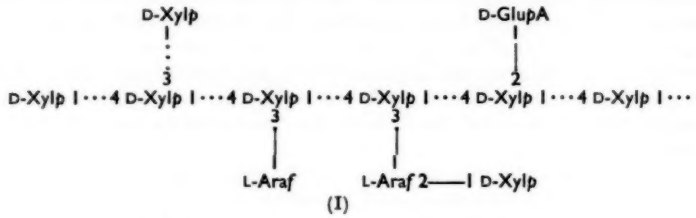
fats and colouring materials and with hot water to remove adhering starch. Extraction of the husks with cold aqueous sodium hydroxide afforded a hemicellulose containing about *ca.* 4% of uronic acid residues. This on hydrolysis gave xylose and arabinose in the ratio of 6 : 1, together with small quantities of acidic oligosaccharides and traces of glucose and galactose. Various attempts to fractionate the polysaccharide failed. A resistant acidic fraction was isolated after vigorous hydrolysis of the polysaccharide; reduction of the derived methyl ester methyl glycoside with potassium borohydride, followed by hydrolysis, gave xylose and glucose with traces of 4-*O*-methylglucose, indicating the presence in the polysaccharide of residues of glucuronic acid (a small proportion as the 4-methyl ether).

The hemicellulose was fully methylated; hydrolysis of the derivative afforded the following, characterised by the formation of crystalline derivatives: 2 : 3 : 4-tri-*O*-methyl-D-xylose (2 parts), 2 : 3-di-*O*-methyl-D-xylose (14 parts), 2-*O*-methyl-D-xylose (3 parts), and 3 : 5-di-*O*-methyl-L-arabinose (1 part). In addition, 2 : 3 : 5-tri-*O*-methyl-L-arabinose (1 part) and an acidic fraction (1 part) were isolated. The arabinose methyl ether was identified by chromatographic mobility and by yielding arabinose on demethylation, optical rotations of mixtures of this sugar and 2 : 3 : 4-tri-*O*-methyl-D-xylose indicating the sugar to be a derivative of L-arabinose. Chromatography of the acidic fraction showed the presence of at least two components, the minor one travelling on the chromatogram at the same rate as 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid. The acidic fraction was converted into the methyl ester methyl glycoside, reduction of which followed by hydrolysis gave 2 : 3 : 4-tri-*O*-methylglucose and 3-*O*-methylxylose in the ratio of 1·2 : 1 together with a trace of 2 : 3-di-*O*-methylxylose. A portion of the reduced acidic fraction was remethylated and after hydrolysis yielded 2 : 3 : 4 : 6-tetra-*O*-methylglucose and 3 : 4-di-*O*-methylxylose. Although insufficient of the acidic fraction was available for the complete characterisation of its hydrolysis products, these observations show that the major component was 3-*O*-methyl-2-*O*-(2 : 3 : 4-tri-*O*-methylglucuronosyl)xylose. It follows from the methylation studies that this polysaccharide contains chains of 1 : 4-linked β-D-xylopyranose units to which are attached at least three types of side-chain, glucuronic acid units directly linked to xylose through position 2, side-chains terminated by L-arabofuranose units and linked to the backbone through position 3 of xylose, and side-chains terminated by D-xylopyranose units and linked to the backbone through position 3 of xylose. It is not possible to decide on the present evidence whether the small amount of D-xylose also isolated from the hydrolysis of the methylated polysaccharide is of structural significance, arising from a double-branching point, or whether the sugar results from incomplete methylation of the polysaccharide or demethylation during hydrolysis.

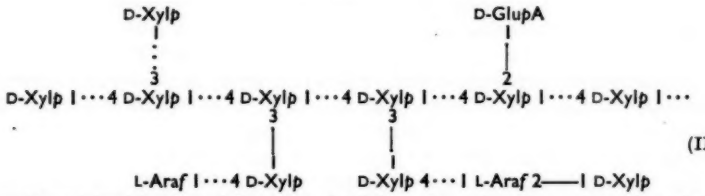
Evidence for the mode of attachment of the non-terminal L-arabofuranose residues follows from the isolation of 2-*O*-D-xylopyranosyl-L-arabinose from the products of mild acid hydrolysis of the polysaccharide. This disaccharide, isolated as the trihydrate, although differing slightly in physical constants from those reported by Whistler and McGilvray,[3] gave an *X*-ray powder photograph identical with that of an authentic sample kindly provided by Dr. D. I. McGilvray. It is probable that the xylopyranose residue of the disaccharide is derived from a non-reducing end-group in the polysaccharide since the disaccharide was released under relatively mild conditions of hydrolysis and no evidence was found for the presence in the hydrolysate of higher oligosaccharides containing arabinose residues. Although it is not possible to advance a unique structure for this hemicellulose, structures (I) and (II) are consistent with the results so far presented. The following evidence, however, shows that at least some terminal L-arabofuranose residues are linked directly to the backbone of D-xylose residues as in structure (I). Hydrolysis of the periodate-oxidised polysaccharide indicated the presence in the polysaccharide of

[3] Whistler and McGilvray, *J. Amer. Chem. Soc.*, 1955, **77**, 2212; see also Whistler and Corbett, *ibid.*, p. 3822.

xylose (21 ± 1·5%) and arabinose (6 ± 0·5%) residues unattacked by periodate. Controlled acid hydrolysis of the polysaccharide under mild conditions resulted in selective hydrolysis of some arabofuranosyl linkages with the formation of a degraded poly-



(I)



(II)

[Sugar residues joined by dotted lines may be linked either directly or through a chain of 1 : 4-linked D-xylopyranose residues].

saccharide. It was not possible, however, to remove all the arabinose residues without extensive hydrolysis of xylopyranosyl linkages. Hydrolysis of the periodate-oxidised degraded polysaccharide indicated the presence therein of xylose (16 ± 1·5%) and arabinose (5 ± 0·5%) residues unattacked by periodate. The decrease in xylose residues unattacked by periodate after selective removal of arabofuranose residues would be expected on the basis of structure (I), whereas no such decrease would result from the removal of arabofuranose residues in structure (II). The proportion of arabinose residues in the degraded polysaccharide, which are unattacked by periodate, indicates that the non-terminal arabofuranosyl linkages are more resistant to acid hydrolysis than terminal arabofuranosyl linkages. Indeed, under the conditions used in the isolation of 2-*O*-D-xylopyranosyl-L-arabinose, the disaccharide was accompanied by appreciable quantities of xylose-containing oligosaccharides. It is not possible, therefore, on the present evidence to decide whether these disaccharide side-chains are also attached directly to the xylan backbone.

A molecular-weight determination by the isothermal-distillation method (by courtesy of Drs. C. T. Greenwood and W. N. Broatch) gave a value of 10,500 ± 500 (degree of polymerisation, 66 ± 3) for the methylated polysaccharide. The methylation analysis indicated the presence of some six non-reducing D-xylopyranose end-groups per molecule; three such end-groups, as shown by the isolation of 2-*O*-D-xylopyranosyl-L-arabinose on partial acid hydrolysis of the original polysaccharide and by the quantity of 3 : 5-di-*O*-methyl-L-arabinose formed on hydrolysis of the methylated polysaccharide, must be linked to the non-terminal arabinose residues. The presence in the molecule, therefore, of three non-reducing D-xylopyranose end-groups linked to other xylose residues indicates some branching in the backbone of D-xylose residues. From the quantity of 2-*O*-methyl-D-xylose formed on hydrolysis of the methylated polysaccharide it is clear that these branch points must involve 1 : 3-linkages.

These results show that this barley husk hemicellulose contains many of the structural features encountered in other polysaccharides of the xylan group.[1] Here, as in the wood xylans and as in several xylans isolated from the Gramineae, glucuronic acid (either unsubstituted or as its 4-methyl ether) is found linked directly to position 2 of a xylose

residue in the backbone of the molecule. Again, terminal non-reducing L-arabofuranose residues, linked to the main chain through $C_{(3)}$ of the xylose residue, are commonly present in polysaccharides of this group. A novel feature of this xylan is the occurrence of non-terminal L-arabofuranose units found in the 2-*O*-D-xylopyranosyl-L-arabofuranose grouping. This disaccharide has been isolated previously from the partial acid hydrolysis of corn cob hemicellulose B;[3] since cleavage of the disaccharide was effected under mild conditions it is probable that in the latter case also this grouping is attached to the backbone of the molecule through an arabofuranosyl linkage. In the barley husk hemicellulose some branching in the backbone of xylose residues is clearly indicated. In the case of several other polysaccharides of this group, however, definite proof of the presence or absence of such branching must await the development of more precise methods of structural analysis.

In the course of the investigation the husk hemicellulose was isolated in a similar way from the corresponding sample of malted barley. A preliminary examination showed that the polysaccharide was qualitatively similar to that isolated from the original barley; thus the same sugar units were present, and chromatography showed that mild acid hydrolysis released arabinose and 2-*O*-xylopyranosylarabinose. Small quantitative differences were shown between the two polysaccharides, *e.g.*, the hemicellulose from the malted barley gave rather less formic acid on periodate oxidation than the barley hemicellulose. The somewhat higher glucosan content in the malted barley polysaccharide probably arose from incomplete removal of starchy polysaccharides since treatment with salivary α-amylase resulted in the formation of glucose and maltose. It is probable, therefore, that only minor changes have taken place in the barley husk hemicellulose during malting.

Experimental

Paper partition chromatography was carried out on Whatman No. 1 filter paper with the following solvent systems (v/v): (*A*) butan-1-ol–benzene–pyridine–water (5 : 1 : 3 : 3, upper layer); (*B*) butan-1-ol–ethanol–water (4 : 1 : 5; upper layer); (*C*) benzene–ethanol–water (169 : 47 : 15; upper layer); (*D*) butan-1-ol–formic acid–water (500 : 115 : 385; upper layer); (*E*) ethyl acetate–pyridine–water (10 : 4 : 3).

Isolation of Barley Husk Hemicellulose.—Barley (Carlsberg variety, harvested in 1953) (10 kg.) in batches (80 g.) was passed through an automatic polishing machine. The husks separated in this manner (*ca.* 10% of the grain) were contaminated with a large amount of starchy powder which was removed by means of a 20 mesh sieve, leaving behind the husk (470 g.) The husks were extracted for 24 hr. with boiling benzene–ethanol (2 : 1) in order to inactivate enzymes and to remove fats and colouring materials. Further extractions with cold water, hot water (75—80°), and with 0·01N-sodium hydroxide (under nitrogen) resulted in complete removal of starch and of water-soluble polysaccharides. The hemicellulose was extracted in the following manner: husks (80 g.) were extracted four times with N-sodium hydroxide (750 ml.), each extraction being carried out for 16 hr. in an atmosphere of nitrogen. The extracts were acidified with glacial acetic acid to pH 4—5 and the polysaccharide was precipitated by addition of acetone (0·8 vol.). The total yield (34 g.) of hemicellulose represented 0·34% by weight of the original barley or 7·2% of the weight of the husk. The polysaccharide had $[\alpha]_D^{16}$ −102° (*c* 0·5 in 0·5N-sodium hydroxide), and chromatographic examination of the hydrolysate by Flood, Hirst, and Jones's[4] method with solvent *A* showed the presence of xylose (67%), arabinose (11%), glucose (2%), and galactose (1%) [Found: ash, 1·2; lignin, 7·8; uronic anhydride (by decarboxylation), 3·7; OMe, 1·2%]. Attempts to fractionate the polysaccharide by precipitation of the copper complex and by precipitation from aqueous solution with ammonium sulphate failed to yield components significantly different in composition.

The polysaccharide (10 g.) was hydrolysed with 2N-sulphuric acid (150 ml.) for 4 hr. at 100°. The solution was neutralised with barium carbonate, the filtrate was concentrated to 50 ml.,

[4] Flood, Hirst, and Jones, *J.*, 1948, 1679.

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barium ions were removed by treatment with Amberlite resin IR-100(H), and the solution was concentrated. The resulting syrup was fractionated on acid-washed charcoal–celite (1 : 1, w/w) (60 × 8 cm.), elution with water yielding monosaccharides and elution with ethyl methyl ketone–water (5 : 95, v/v) yielding acidic oligosaccharides together with some neutral sugars (50 mg.). Further fractionation on filter sheets with solvent *A* afforded an acidic oligosaccharide (17 mg.) and a trace of an unidentified sugar. The acidic component was converted into the methyl ester methyl glycoside, reduced with potassium borohydride, and hydrolysed, chromatography showing approximately equal amounts of xylose and glucose, and a trace of 4-*O*-methylglucose.

Methylation of Barley Husk Hemicellulose.—The polysaccharide (10 g.) was methylated by successive additions of methyl sulphate and sodium hydroxide, and then with methyl iodide and silver oxide. The product (6·5 g.) was fractionated by precipitation from chloroform with light petroleum (b. p. 60—80°), giving two main fractions: **1**, precipitated with 3 vol. of light petroleum {4·2 g.; $[\alpha]_D$ −92° ($CHCl_3$); OMe, 38·7%}, and **2**, precipitated with 4 vol. of light petroleum {1·6 g.; $[\alpha]_D$ −95° ($CHCl_3$); OMe, 38·7%}; these fractions were combined and were used in subsequent experiments.

Hydrolysis of Methylated Hemicellulose and Separation of Methylated Sugars.—The methylated polysaccharide (4·4 g.) was hydrolysed successively with boiling methanolic 3% hydrogen chloride (500 ml.) for 2·5 hr. and with 0·5N-hydrochloric acid (500 ml.) at 100° for 4·5 hr. A small quantity (0·12 g.) of insoluble material was separated at this stage; further hydrolysis yielded no detectable sugars [Found: OMe, 31·0; lignin, 80%]. Evaporation after neutralisation with silver carbonate yielded a syrup (4·3 g.), which was treated (in aqueous solution) with barium carbonate (0·2 g.). The mixture of methylated sugars (4·02 g.) was fractionated on cellulose (90 × 3 cm.) by elution with light petroleum (b. p. 100—120°)–butan-1-ol (7 : 3) saturated with water, butan-1-ol partly saturated with water, and with water to give nine fractions.

Fraction **1**. The sugar (34 mg.) travelled on the chromatogram in solvent *B* at the same rate as 2 : 3 : 5-tri-*O*-methyl-L-arabinose and/or 2 : 3 : 4-tri-*O*-methyl-D-xylose. Demethylation showed only arabinose, and chromatography in solvent *C* showed only tri-*O*-methylarabinose (Found: OMe, 48·2. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). Attempts to prepare crystalline derivatives failed.

Fractions **2** *and* **3**. Chromatography showed that both these fractions (79 and 270 mg.) contained mixtures of 2 : 3 : 5-tri-*O*-methylarabinose and 2 : 3 : 4-tri-*O*-methylxylose. Calculations from the observed optical rotations, $[\alpha]_D$ −31° and +9° (H_2O), indicated that fractions 2 and 3 contained 86% and 19% respectively, of 2 : 3 : 5-tri-*O*-methyl-L-arabinose {2 : 3 : 5-tri-*O*-methyl-L-arabinose has $[\alpha]_D$ −39·5° (H_2O), and 2 : 3 : 4-tri-*O*-methyl-D-xylose has $[\alpha]_D$ +20° (H_2O)}.

Fraction **4**. The sugar (80 mg.) travelled on the chromatogram in solvents *B* and *C* at the same rate as 2 : 3 : 4-tri-*O*-methyl-D-xylose and slowly crystallised (Found: OMe, 48·2. Calc. for $C_8H_{16}O_5$: OMe, 48·4%). After recrystallisation from acetone–light petroleum the sugar had m. p. and mixed m. p. 87—89° and $[\alpha]_D$ +64·5° (2 min.) ⟶ +20° (80 min., const.) (*c* 0·6 in H_2O). The derived 2 : 3 : 4-tri-*O*-methyl-*N*-phenyl-D-xylosylamine had m. p. and mixed m. p. 100—101°.

Fraction **5**. The syrup (141 mg.) had $[\alpha]_D$ −16° (*c* 0·6 in H_2O) (Found: OMe, 35·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%) and on demethylation yielded arabinose. Its rate of movement on the chromatogram in solvent *B* was the same as that of 2 : 5-di-*O*-methyl-L-arabinose, but the brown coloration (and yellow fluorescence in ultraviolet light) with aniline oxalate differed markedly from the grey coloration (and pink fluorescence in ultraviolet light) given by the 2 : 5-isomer. The sugar was further distinguished from the 2 : 5-dimethyl ether by its considerably greater ionophoretic mobility. The sugar was identified as 3 : 5-di-*O*-methyl-L-arabinose by conversion into 3 : 5-di-*O*-methyl-L-arabonolactone, m. p. 68—71°, which gave an *X*-ray powder photograph (by courtesy of Dr. C. A. Beevers) identical with that of an authentic specimen, and into 3 : 5-di-*O*-methyl-L-arabonamide, identified by its m. p. and mixed m. p. 144·5—145° and by its *X*-ray powder photograph.

Fraction **6**. The syrup (2·113 g.) crystallised when seeded with 2 : 3-di-*O*-methyl-β-D-xylose and had m. p. and mixed m. p. 81—83° and $[\alpha]_D^{17}$ −20·6° (4 min.) ⟶ +24·9° (65 min., const.) (*c* 1·2 in H_2O) (Found: OMe, 35·0. Calc. for $C_7H_{14}O_5$: OMe, 34·8%). The identity of the sugar was confirmed by its conversion into 2 : 3-di-*O*-methyl-*N*-phenyl-D-xylosylamine,

m. p. and mixed m. p. 123—124°, and into 2 : 3-di-*O*-methyl-D-xylonamide, m. p. and mixed m. p. 133—134°.

Fraction 7. The syrup (412 mg.) slowly yielded a crystalline sugar together with a small quantity of syrup. The crystalline material was ionophoretically pure 2-*O*-methylxylose; the syrupy material contained mainly the 2-methyl ether with a trace of the 3-methyl ether. Recrystallisation afforded 2-*O*-methyl-β-D-xylose, m. p. and mixed m. p. 133—134°, $[\alpha]_D^{17}$ −5·6° ⟶ +34·4° (90 min., const.) (*c* 1·4 in H_2O) (Found: OMe, 19·1. Calc. for $C_6H_{12}O_5$: OMe, 18·9%). The derived 2-*O*-methyl-*N*-phenyl-D-xylosylamine had m. p. and mixed m. p. 125—126°.

Fraction 8. The sugar (34 mg.) had m. p. 140—142° and mixed m. p. (with D-xylose) 141—144°, and gave an *X*-ray powder photograph identical with that of D-xylose.

Fraction 9. The fraction (259 mg.) obtained by elution of the cellulose with water was purified by solution in hot methanol, and after removal of barium ions by treatment with Amberlite resin IR-120(H) yielded a syrup (154 mg.), $[\alpha]_D^{17}$ +96° (H_2O) (Found: OMe, 29·6. Calc. for a tetra-*O*-methylaldobiouronic acid, $C_{15}H_{26}O_{11}$: OMe, 32·4%). Chromatography in solvent *D* showed two components, the minor and faster-moving one travelling at the same rate as 2 : 3 : 4-tri-*O*-methyl-D-glucuronic acid. On further hydrolysis the slower-moving component decreased in amount with the formation of more tri-*O*-methylglucuronic acid and of a mono-*O*-methylxylose. Some of the acidic fraction (50 mg.) was converted into the methyl ester methyl glycoside by refluxing it with methanolic 1% hydrogen chloride (25 ml.) for 6 hr. The product was dissolved in dry ether (25 ml.), and lithium aluminium hydride (50 mg.) was added slowly during 3 hr. to the boiling solution. Water was added to the cooled solution to destroy excess of hydride, and the mixture was acidified with sulphuric acid and extracted with chloroform. Hydrolysis of the extract with N-sulphuric acid for 5 hr. at 100° yielded two main components *a* and *b* together with a trace of 2 : 3-di-*O*-methylxylose. Quantitative determination showed that fractions *a* and *b* were present in the ratio of 1 : 1·2. Fraction *a* travelled on the chromatogram in solvent *B* at the same rate as 2- and/or 3-*O*-methyl-D-xylose; paper ionophoresis showed that the fraction was mainly 3-*O*-methylxylose with only a trace of the 2-methyl ether. Fraction *b* travelled on the chromatogram at the same rate as 2 : 3 : 4-tri-*O*-methyl-D-glucose and gave glucose on demethylation.

Another portion of the acidic fraction (30 mg.) was converted into the methyl ester methyl glycoside and reduced with lithium aluminium hydride as described previously. The reduction product was methylated with methyl iodide and silver oxide and the methylated disaccharide was hydrolysed with 2N-hydrochloric acid for 4 hr. at 100° yielding two sugars *c* and *d*. In solvent *B* sugar *c* travelled on the chromatogram slightly more slowly than 2 : 3-di-*O*-methyl-D-xylose and at a rate corresponding to 3 : 4-di-*O*-methylxylose. The ionophoretic mobility of sugar *c* was considerably greater than that of 2 : 3-di-*O*-methylxylose as would be expected for the 3 : 4-dimethyl ether. Sugar *d* was chromatographically indistinguishable from 2 : 3 : 4 : 6-tetra-*O*-methylglucose; a small sample was obtained crystalline, m. p. 76—84°

Partial Acid Hydrolysis of Hemicellulose and Isolation of 2-O-D-*Xylopyranosyl*-L-*arabinose.*—Barley husk hemicellulose (13 g.) was heated in aqueous 0·02N-oxalic acid (1·3 l.) at 96° for 3·5 hr. The cooled solution was neutralised with calcium carbonate, filtered, concentrated, and poured into ethanol (10 vol.) to precipitate material of high molecular weight. The supernatant liquid was concentrated to a syrup (*ca.* 3 g.) which was fractionated on charcoal–celite (1 : 1, w/w) (25 × 4 cm.), elution with water giving monosaccharides (1·7 g.), and elution with ethanol–water (5 : 95) giving fractions (i) (0·39 g.) and (ii) (0·145 g.). Fraction (i) contained a major component with R_{xylose} 0·67 in solvent *E* and a minor component with R_{xylose} 0·59, travelling at the same rate as xylobiose. Fraction (ii) contained the same two components (mainly xylobiose) together with traces of slower-moving oligosaccharides having R_{xylose} 0·40, 0·28, and 0·14. The main component from fraction (i) crystallised readily and after several recrystallisations from ethanol–water had m. p. 97—98°, $[\alpha]_D^{19}$ +53·7° (6 min.) ⟶ +33·2° (2 hr., const.) (*c* 1·3 in H_2O) (Found: C, 36·1; H, 7·0. Calc. for $C_{10}H_{18}O_9,3H_2O$: C, 35·7; H, 7·2%). A molecular-weight determination from a single crystal *X*-ray photograph and a density measurement (kindly carried out by Mr. H. W. Erhlich) gave a value of 333 ± 6 (calc. for a disaccharide trihydrate, 336). Hydrolysis of the sugar gave xylose and arabinose, but after oxidation with bromine water hydrolysis gave only xylose. The sugar was chromatographically indistinguishable from and gave an *X*-ray powder photograph identical with that of 2-*O*-D-xylopyranosyl-L-arabinose.

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Periodate Oxidation of Hemicellulose.—Hemicellulose (269 mg.) was dissolved in potassium chloride solution (0·56M; 60 ml.), and sodium metaperiodate (0·2M; 20 ml.) was added. The formic acid released, estimated by Anderson, Greenwood, and Hirst's method,[5] reached a constant value of 0·10 mole per pentose residue after 7 days. Oxidation of the polysaccharide with sodium metaperiodate solution indicated a consumption of periodate of 0·85 mole per pentose residue (constant after 2 days).

Estimation of Sugar Residues Unattacked by Periodate.—The polysaccharide (0·5 g.) in sodium metaperiodate solution (0·2M, 25 ml.) was set aside for 54 hr. Periodate and iodate ions were precipitated by the addition of barium chloride solution and the resulting solution was dialysed against distilled water for 3 days; concentration and precipitation with acetone afforded the periodate-oxidised polysaccharide (0·25 g.). Hydrolysis of this material and chromatographic examination of the hydrolysate,[4] using galactose as reference sugar, showed the presence of xylose (21 $\pm$ 1·5%) and arabinose (6 $\pm$ 0·5%).

The hemicellulose (0·8 g.) was heated with aqueous oxalic acid (0·02N; 80 ml.) at 96° for 1 hr. (these represent optimun conditions for the removal of arabinose residues without extensive degradation of the molecule). The cooled solution was neutralised with calcium carbonate, and the centrifugate was poured into acetone (10 vol.) to precipitate degraded polysaccharide. The mother liquor was concentrated and sugars (0·057 g.) were extracted with boiling methanol. Quantitative chromatography showed the presence in the methanol extract of arabinose and xylose in the ratio of 11 : 1 together with traces of xylosylarabinose and other oligosaccharides. The degraded hemicellulose was converted into the corresponding periodate-oxidised polysaccharide, hydrolysis of which afforded xylose (16 $\pm$ 1·5%) and arabinose (5 $\pm$ 0·5%) (these figures are expressed as percentages of the original hemicellulose).

Husk Hemicellulose from Malted Barley.—Malted barley (Carlsberg variety, harvested in 1953) (700 g.) was given a rapid treatment in an automatic milling machine, and most of the husks were removed from the fragmented grain particles. The husks (63 g.) were extracted in the manner described previously except that four extractions with hot water for 8 hr. each were required to remove the adhering starch. Alkaline extraction afforded hemicellulose (6·2 g.), which was further extracted with boiling ethanol–water (4 : 1) to ensure complete removal of contaminating sugars. The hemicellulose had $[\alpha]_D$ −81° (*c* 0·5 in 0·5N-NaOH) and gave on hydrolysis xylose, arabinose, and glucose in the ratio of 76 : 16 : 8. Digestion of a 1% solution of the polysaccharide with salivary α-amylase in phosphate–citrate buffer at pH 6·8 at 35° followed by chromatographic examination of the hydrolysate showed that maltose and glucose were formed. Partial acid hydrolysis of the polysaccharide yielded arabinose and xylopyranosylarabinose, together with traces of xylose and xylose-containing oligosaccharides. A sample of the hemicellulose was oxidised with potassium metaperiodate, and the formic acid released [5] reached a constant value of 0·09 mole per pentose residue after 11 days.

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[5] Anderson, Greenwood, and Hirst, *J.*, 1955, 225.

841. *Reactions of Unsaturated Compounds. Part XIII.* The Oxidation of 1 : 1-Diarylolefins by Chromic Oxide.*

By W. J. Hickinbottom and G. E. M. Moussa.

The oxidation of 2-methyl-1 : 1-diphenylprop-1-ene by chromic oxide in acetic anhydride gives 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane with small amounts of fission products. 2-Methyl-1 : 1-di-*p*-tolyl-, 1 : 1-di-*p*-chlorophenyl-2-methyl-, and 1 : 1-di-*p*-bromophenyl-2-methyl-prop-1-ene yield crystalline epoxides in satisfactory yield under similar conditions. 2 : 3-Dimethyl-1 : 1-diphenylbut-1-ene is similarly oxidised. The epoxides are relatively stable towards aqueous sulphuric acid.

Chromic acid in aqueous sulphuric acid brings about oxidative fission of the double bond without any rearrangement.

The significance of these results is discussed.

In earlier papers it has been shown that many alkyl-substituted olefins are oxidised by chromic oxide in acetic anhydride to the corresponding epoxides, in yields depending on the structure of the olefin. This paper reports an extension of the investigation to some diarylolefins. Epoxide was the major product from all the olefins examined, but fission products were also obtained. One of the olefins, 2 : 3-dimethyl-1 : 1-diphenylbut-1-ene also gave a small amount of an unsaturated aldehyde as the result of oxidation of a α-methylene group. The results are summarised in the Table, together with the effect of chromic acid in aqueous sulphuric acid.

	Product of the action of	
	CrO_3–Ac_2O	CrO_3–aq. H_2SO_4
$CMe_2{=}CPh_2$	Epoxide 88%; acetone; benzophenone	Benzophenone; acetone
$CMe_2{=}C(C_6H_4Me\text{-}p)_2$	Epoxide 60%; acetone; di-*p*-tolyl ketone	Di-*p*-tolyl ketone; acetone
$CMe_2{=}C(C_6H_4Br\text{-}p)_2$	Epoxide 64%; acetone; di-*p*-bromobenzophenone	Di-*p*-bromobenzophenone; acetone
$CMe_2{=}C(C_6H_4Cl\text{-}p)_2$	Epoxide 30%; acetone; di-*p*-chlorobenzophenone	Di-*p*-chlorobenzophenone; acetone
$Pr^iMeC{=}CPh_2$	Epoxide; acetone; benzophenone; *iso*butyric acid; 3 : 3-diphenyl-2-*iso*propylprop-2-enal	Benzophenone; *iso*butyric acid; acetone; a keto-acid

The epoxides obtained in the chromic oxidation are crystalline and were identified by comparison with those obtained by the action of perbenzoic acid. They are relatively stable to aqueous sulphuric acid: those from 2-methyl-1 : 1-diphenyl- and -1 : 1-di-*p*-tolyl-prop-1-ene are slowly converted into the corresponding glycols by agitation with cold 43% sulphuric acid. The epoxides from the other olefins are not appreciably attacked by acid of this concentration even after 3 days. Acid of this concentration was used as the medium for chromic acid oxidation, so epoxides can no longer be considered as the true intermediates. The simplest and, at present, most satisfactory view of the course of the oxidation is to assume some intermediate formed by addition of chromic acid or chromic oxide to the double bond. It is only by such an assumption that the rearrangements observed in aqueous sulphuric can be correlated with the formation of epoxides in acetic anhydride. The intermediate in anhydrous solvents can split out CrO_2 to give an epoxide; in aqueous sulphuric acid, either hydrolysis and oxidation or rearrangement may occur according to the concentration of sulphuric acid. Such intermediates may well result by electrophilic addition of chromic oxide (Hickinbottom and Peters [1]) or from cyclic compounds of the type postulated by Zeiss and Zwanzig.[2]

* Part XII, *J.*, 1955, 1360.

[1] Hickinbottom and Peters, *J.*, 1955, 1360.

[2] Zeiss and Zwanzig, *Chem. and Ind.*, 1956, 545; *J. Amer. Chem. Soc.*, 1957, **79**, 1733.

Experimental

Concentrations of sulphuric acid are expressed in g. of acid per 100 g. of solution.

2-*Methyl*-1 : 1-*diphenylprop*-1-*ene*.—2-Methyl-1 : 1-diphenylpropan-1-ol was dehydrated by heating it with phthalic anhydride (50% yield) or with acetic anhydride (60% yield); but the most satisfactory conditions consisted in keeping the alcohol (40 g.), pyridine (50 g.), and phosphorus oxychloride (42 g.) at room temperature for several days. The olefin was isolated by pouring the mixture on ice, extracting it with ether, washing the ether solution with sodium carbonate solution and dilute hydrochloric acid, then drying and distilling it. Refluxing with sodium for 6 hr. then gave a product of b. p. 114°/1·6 mm., $n_D^{23\cdot5}$ 1·586 (Found: C, 92·5; H, 7·6. Calc. for $C_{16}H_{16}$: C, 92·3; H, 7·7%). Sabatier and Murat [3] give b. p. 293°, n_D^{16} 1·596.

Oxidation by chromic oxide. Chromic oxide (15 g.) in acetic anhydride (80 c.c.) was added during 0·5 hr. to a stirred, cooled solution of 2-methyl-1 : 1-diphenylprop-1-ene (20 g.) in acetic anhydride (100 c.c.). Stirring was then continued for 3 hr. The mixture was then poured into ice-water (1·5 l.), and the product isolated by ether. Drying and distillation of the ether solution, after it had been washed with aqueous sodium carbonate, gave the main product, b. p. 102—112°/0·7 mm. (14·4 g.). This solidified, and consisted essentially of 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane. Purified by trituration with alcohol and crystallisation from the same solvent, it had m. p. 64° (Found: C, 85·6; H, 7·1. Calc. for $C_{16}H_{16}O$: C, 85·7; H, 7·1%). Ramart-Lucas [3] gives m. p. 61—62°.

From the alcoholic liquors benzophenone was isolated as 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242—243°. Acetone was identified in the aqueous washings of the crude ether extract.

For comparison, 1 : 2-epoxy-2-methyl-1 : 1-diphenylpropane was prepared by reaction of the olefin with benzoyl peroxide, then having b. p. 88°/0·25 mm., m. p. and mixed m. p. 64°.

The epoxide (0·2 g.) was shaken in suspension in aqueous sulphuric acid (5 c.c.; 43%) for several days. The diol, crystallised from light petroleum (b. p. <40°), had m. p. 94—95° (Ramart-Lucas [4] gives m. p. 91°); benzophenone was obtained by oxidation with aqueous periodic acid.

Oxidation by chromic acid in aqueous sulphuric acid. To a stirred suspension of 2-methyl-1 : 1-diphenylprop-1-ene (20 g.) in aqueous sulphuric acid (110 c.c.; 65%), chromic oxide (30 g.) in water (46 c.c.) was added continuously during 15 min. The ensuing vigorous reaction was controlled by cooling the flask with alcohol–solid carbon dioxide. Stirring was continued for 3 hr. after all the oxidising agent had been added. Next morning the mixture was diluted with water and extracted with ether. From the ether extract, washed with aqueous sodium carbonate, benzophenone (11·5 g.), m. p. and mixed m. p. 49° (from alcohol), was obtained. Steam-distillation of the alkaline washings of the ether extract gave acetone (1·2 g., estimated by Messinger's method).

2-*Methyl*-1 : 1-*di*-p-*tolylprop*-1-*ene*.—2-Methyl-1 : 1-di-*p*-tolylpropan-1-ol, m. p. 95°, was prepared as described by Schlenk and Bergmann [5] who give m. p. 99°. It was dehydrated to 2-methyl-1 : 1-di-*p*-tolylprop-1-ene by saturating it with hydrogen chloride in ethereal solution, and treating the resulting chloro-compound with pyridine. The olefin, crystallised from methyl alcohol, melts at 50° (Schlenk and Bergmann [5] give m. p. 50°) (Found: C, 91·2; H, 8·4. Calc. for $C_{18}H_{20}$: C, 91·5; H, 8·5%).

Oxidation by chromic oxide in acetic anhydride. The olefin (20 g.) in acetic anhydride (100 c.c.) was oxidised by chromic oxide (11 g.) in acetic anhydride (120 c.c.) as above except that the addition of the oxidising agent required 80 min. and the mixture was kept overnight. Distillation of the neutral product gave 1 : 2-epoxy-2-methyl-1 : 1-di-*p*-tolylpropane (13 g.), b. p. 139—142°/1·5—1·7 mm., m. p. and mixed m. p. 58—59° (from alcohol), and a fraction (1 g.), b. p. 142/1·5 mm., containing di-*p*-tolyl ketone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229°). The aqueous washings of the crude product contained acetone.

The *epoxide* was also prepared from the olefin and perbenzoic acid in chloroform; crystallised from alcohol it melted at 58—59° (Found: C, 85·6; H, 8·0. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

[3] Sabatier and Murat, *Compt. rend.*, 1913, **156**, 1433.
[4] Ramart-Lucas, *Bull. Soc. chim. France*, 1929, **45**, 718.
[5] Schlenk and Bergmann, *Annalen*, 1930, **479**, 49.

It is hydrated by cold 43% sulphuric acid to give a glycol, identified by oxidation with periodic acid to di-*p*-tolyl ketone, m. p. and mixed m. p. 94—95° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 229°).

Oxidation by chromic acid in aqueous sulphuric acid. 2-Methyl-1 : 1-di-*p*-tolylprop-1-ene (4 g.), suspended in 65% sulphuric acid (22 c.c.) and oxidised by chromic oxide (2·6 g.) in water (9·2 c.c.), gave di-*p*-tolyl ketone, m. p. and mixed m. p. 94—95° (3 g.), and acetone (0·29 g.).

1 : 1-*Di*-p-*bromophenyl*-2-*methylprop*-1-*ene*.—1 : 1-Di-*p*-bromophenyl-2-methylpropan-1-ol was obtained by reaction of ethyl *iso*butyrate (110 g.) with the Grignard reagent from *p*-dibromobenzene (500 g.) and magnesium (60 g.). The crude alcohol, distilled under reduced pressure, gave 1 : 1-di-*p*-bromophenyl-2-methylprop-1-ene (52 g.), b. p. 174°/0·7 mm., m. p. 97° (from alcohol) (Ashley *et al.*[6] give m. p. 96°). A sticky polymer remained as residue.

Oxidation by chromic oxide. The olefin (15 g.) in acetic anhydride (150 c.c.) was oxidised by chromic oxide (5·2 g.) in acetic anhydride (80 c.c.). The ether solution of the neutral products deposited 4 : 4′-dibromobenzophenone (3 g.), m. p. and mixed m. p. 176°, on concentration. The remainder of the neutral product was distilled, to give 1 : 1-di-*p*-bromophenyl-1 : 2-epoxy-2-methylpropane (10 g.), b. p. 177—178°/1·2 mm., m. p. 94—95° (from alcohol). Distillation of the aqueous-alkaline washings of the crude product gave acetone. No acidic products were recognised.

The *epoxide* was also prepared from the olefin and perbenzoic acid. After crystallisation from alcohol it had m. p. and mixed m. p. 94° (Found: C, 50·6; H, 3·6; Br, 41·3. $C_{16}H_{14}OBr_2$ requires C, 50·3; H, 3·7; Br, 41·8%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (10 g.) in 65% sulphuric acid (55 c.c.), oxidised by chromic oxide (4·2 g.) in water (23 c.c.) at room temperature for 4 days, gave 4 : 4′-dibromobenzophenone (8·5 g.), m. p. and mixed m. p. 176° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 263—265°). Acetone (0·29 g.) was identified in the aqueous-alkaline washings.

1 : 1-*Di*-p-*chlorophenyl*-2-*methylprop*-1-*ene*.—1 : 1-Di-*p*-chlorophenyl-2-methylpropan-1-ol (290 g.), m. p. 115° (Skerrett and Woodcock [7] record m. p. 115—116°), was prepared from ethyl *iso*butyrate (135 g.), *p*-bromochlorobenzene (500 g.), and magnesium (70 g.). It was converted, as described for 2-methyl-1 : 1-di-*p*-tolylpropan-1-ol, into 1 : 1-di-*p*-chlorophenyl-2-methylprop-1-ene (125 g.), b. p. 132°/0·2 mm., m. p. 71—72° (Found: C, 69·6; H, 4·9; Cl, 25·4. Calc. for $C_{16}H_{14}Cl_2$: C, 69·3; H, 5·1; Cl, 25·6%). Skerrett and Woodcock [7] give m. p. 69—70°.

Oxidation with chromic oxide. The olefin (20 g.) with chromic oxide (9·1 g.) in acetic anhydride gave 4 : 4′-dichlorobenzophenone (3 g.), m. p. and mixed m. p. 238—240°, acetone (0·27 g.), and 1 : 1-di-*p*-chlorophenyl-1 : 2-epoxy-2-methylpropane (6 g.), m. p. and mixed m. p. 57—58°, b. p. 148—150°/0·65 mm.

The *epoxide*, prepared by perbenzoic acid, had m. p. and mixed m. p. 57—58° (Found: C, 65·4; H, 4·9; Cl, 23·5. $C_{16}H_{14}OCl_2$ requires C, 65·5; H, 4·8; Cl, 24·2%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (15 g.), 65% sulphuric acid (82·5 c.c.), chromic oxide (8·5 g.), and water (34·5 c.c.) gave 4 : 4′-dichlorobenzophenone (3·7 g.), m. p. and mixed m. p. 145° (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 238—240°), acetone (0·3 g.), and some unchanged olefin.

2 : 3-*Dimethyl*-1 : 1-*diphenylbut*-1-*ene*.—Refluxing 2 : 3-dimethyl-1 : 1-diphenylbutan-1-ol (205 g.) with phthalic anhydride (600 g.) for several hours gave 2 : 3-*dimethyl*-1 : 1-*diphenylbut*-1-*ene*, b. p. 168—170/15 mm., n_D^{15} 1·5740 (94·4 g.) (Found: C, 91·2; H, 8·4. $C_{18}H_{20}$ requires C, 91·5; H, 8·5%).

The *alcohol* (240 g.), b. p. 198—200/15 mm., n_D^{17} 1·564, was obtained from ethyl αβ-dimethylbutyrate (147·5 g.) and phenylmagnesium bromide (from bromobenzene, 490 g., and magnesium, 75 g.) (Found: C, 84·85; H, 8·7. $C_{18}H_{22}O$ requires C, 85·0; H, 8·7%).

αβ-Dimethylbutyric acid, b. p. 188°, n_D^{19} 1·4120, was prepared from ethyl methyl*iso*propylmalonate, b. p. 142—146°, n_D^{20} 1·4023.

Oxidation by chromic oxide. The olefin (10 g.) in acetic anhydride (50 c.c.) was oxidised by chromic oxide (5·2 g.) in acetic anhydride (50 c.c.). Distillation of the neutral product gave main fractions: (*a*) b. p. 164—170°/11—13 mm.; (*b*) 170—172°/12 mm.; (*c*) 180—190°/12 mm.; (*d*) 190—212°/11—12 mm. Fractions (*a*) and (*b*), triturated with alcohol, gave 1 : 2-epoxy-2 : 3-dimethyl-1 : 1-diphenylbutane, m. p. 93°. A further small amount of the epoxide was

[6] Ashley, Grove, and Henshall, *J.*, 1948, 261.
[7] Skerrett and Woodcock, *J.*, 1950, 2718.

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obtained from (*c*). From the alcoholic solutions remaining after these crystallisations, benzophenone was isolated as its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242°. Fraction (*d*) reduced permanganate and gave a red 2 : 4-dinitrophenylhydrazone, m. p. 186—187° (from alcohol–ethyl acetate) (Found: C, 66·4; H, 4·95; N, 13·1. $C_{24}H_{22}O_4N_4$ requires C, 67·0; H, 5·1; N, 13·0%). The colour and the analysis suggest that this is the 2 : 4-*dinitrophenylhydrazone* of 3 : 3-diphenyl-2-*iso*propylprop-2-enal. From the alkaline washings of the crude oxidation product, acetone and *iso*butyric acid (*S*-benzylthiuronium salt, m. p. and mixed m. p. 143°) were obtained.

The *epoxide*, b. p. 172—174°/12 mm., was also prepared by perbenzoic acid. Crystallised from ethyl alcohol, it had m. p. and mixed m. p. 93° (Found: C, 85·8; H, 8·0. $C_{18}H_{20}O$ requires C, 85·7; H, 8·0%).

Oxidation by chromic acid in aqueous sulphuric acid. The olefin (10 g.) in 65% sulphuric acid (55 c.c.) was oxidised by chromic oxide (6·4 g.) in water (23 c.c.). The neutral product consisted of benzophenone (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 242°). The alkaline aqueous washings of the crude product contained acetone, *iso*butyric acid, and a small amount of a *keto-acid*, m. p. 199—200° (Found: C, 76·0; H, 6·1. $C_{18}H_{18}O_3$ requires C, 76·6; H, 6·4%) (2 : 4-dinitrophenylhydrazone, m. p. 115—117°).

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842. *Nitramines and Nitramides. Part XI.* The Acid-catalysed Decomposition of Various* ON-*Dialkylnitramines.*

By PETER BRUCK and ALEX. H. LAMBERTON.

It appears that the acid-catalysed decomposition of R·N:NO·OR′ (R and R′ being alkyl groups) proceeds by scission of the R–N and N–OR′ bonds. Electron donation by R strongly favours decomposition; with R′ constant the relative rates are R = Me < Et < *neo*-C_5H_{11} < $Pr^i \ll Bu^t$. With R constant, changes in R′ act mildly in the opposite direction. Some of the activation energies concerned have been measured. Water molecules are not covalently involved in the transition state, since the rate of decomposition of Me·N:NO·OMe in suitable conditions is proportional to the acidity function h_0, rather than to $[H_3O^+]$.

The bond-scissions may occur essentially in one stage, or successively: if successively, the apparent influence of both R and R′ shows the first scission to be rate-determining.

We include a brief discussion of these, and earlier, observations regarding the stability of aliphatic *N*-nitro-compounds towards acids.

IN an earlier paper of this series [1] we investigated the acid-catalysed hydrolysis of *ON*-dialkylnitramines ($R{\cdot}N{:}NO{\cdot}OR' + H_2O \longrightarrow ROH + N_2O + R'OH$) by an examination of the *O*-methyl-*N*-*iso*propyl compound. It was shown, experimentally, and to a small extent by consideration of work of long standing in the literature, that : (1) the reaction did not proceed by way of the primary nitramine ($Pr^i{\cdot}NH{\cdot}NO_2$), and probably involved scission of the alkyl–nitrogen bond to yield Pr^{i+}; (2) the rate of decomposition was proportional to $[H^+][Pr^i{\cdot}N{:}NO{\cdot}OMe]$ over a 2000-fold range of concentration of hydrochloric acid; and (3) the reaction exhibited general acid-catalysis, since acetic acid had a catalytic effect additional to that dependent upon its ionisation. In a subsequent paper [2] further evidence was given for the production of alkyl cations by the heterolysis of the alkyl–nitrogen bond in primary nitramines and *ON*-dialkylnitramines.

* Part X, *J.*, 1956, 921.

[1] Bruck and Lamberton, *J.*, 1955, 3997.
[2] Bruck, Denton, and Lamberton, *J.*, 1956, 921.

Scission of the molecules $R{\cdot}NH{\cdot}NO_2$ or $R{\cdot}N{:}NO{\cdot}OR'$ thus occurs at the R–N bond, but another rupture is required to yield nitrous oxide, which is produced from both types of compound. By analogy with the acid-catalysed hydrolysis of esters,[3] this second rupture might occur in the dialkyl compounds at either the O–R′ or the N–OR′ bonds; for various reasons the possibility of O–R′ rupture can now be eliminated. In the first place, such a split would not lead directly to nitrous oxide, as does the breaking of the N–OR′ (and R–N) bonds. Secondly, the removal of R′ alone would give rise to the primary nitramine $R{\cdot}NH{\cdot}NO_2$ by such a route as $R{\cdot}N{:}NO{\cdot}OR' \xrightarrow{+H^+} R{\cdot}N{:}NO{\cdot}\overset{+}{O}HR' \xrightarrow{-R'^+} R{\cdot}N{:}NO{\cdot}OH \rightleftharpoons R{\cdot}NH{\cdot}NO_2$; and there is no evidence of the production of either the cation R'^+ or the nitramine $R{\cdot}NH{\cdot}NO_2$. In our earlier paper [1] we stated this argument in more detail, and showed that *O*-methyl-*N*-*iso*propylnitramine did not yield *iso*propylnitramine in the course of decomposition. We have now examined *N*-methyl-*O*-*iso*propylnitramine (in which O–R′ fission would be facilitated by electron donation from the *iso*propyl group), but again decomposition does not proceed by way of hydrolysis to the primary nitramine. Further, the acid-catalysed decompositions of primary nitramines and of *ON*-dialkylnitramines are presumably closely allied, and O–H bond fission of the *aci*-form of a primary nitramine ($R{\cdot}N{:}NO{\cdot}OH$) would be meaningless from the point of view of decomposition.

Finally, we have obtained positive evidence of N–OR′ bond fission by preparing and decomposing (+)-*O*-*sec*.-butyl-*N*-methylnitramine; the reaction cycle (+)-$Bu^sOH \longrightarrow$ (−)-$Bu^sBr \longrightarrow$ (+)-$Me{\cdot}N{:}NO{\cdot}OBu^s \longrightarrow$ (+)-Bu^sOH was performed with at least 56% retention of optical activity. Since considerable racemisation is known to occur on conversion of *sec*.-butyl alcohol into the bromide, the overall retention of 56% of the activity left little scope for racemisation at other stages, and the final decomposition must be highly stereospecific. This conclusion strongly favours scission of the N–OBu^s bond.

The mechanism of the reaction has been further studied by the extension of our previous work [1] on *O*-methyl-*N*-*iso*propylnitramine to a variety of *ON*-dialkylnitramines, and our results are presented in Tables 1 and 2. The rates of decomposition have been measured manometrically, or by observation of optical density in the ultraviolet region. These methods, based respectively on the appearance of the final product (Gas), and the disappearance of the nitramine (U.V.), had already been shown [1] to be in agreement for *O*-methyl-*N*-*iso*propylnitramine: whenever both methods were used on one compound the results now reported confirm (though see footnote to Table 1) our previous observations. Again, in accordance with the behaviour of *O*-methyl-*N*-*iso*propylnitramine, the rates of decomposition of all the compounds investigated were proportional to $[H^+][R{\cdot}N{:}NO{\cdot}OR']$. The second-order rate coefficients are reported as the catalytic constants, k_{H^+}; though the results given later in Table 5 also show that, where there is a difference, the proportionality is to the acidity function h_0, rather than to $[H^+]$. The lines obtained by plotting the first-order rate coefficients in Table 1 against the acid concentration all converge on the origin; there is thus no appreciable catalysis by water at 45°.

Inspection of Table 1 shows that the k_{H^+} values fall into three main groups: those for the *N*-ethyl compounds are approximately 10 times, and those for the *N*-*iso*propyl compounds nearly 100 times as great as the values obtained for the *N*-methyl compounds. The values given in Table 2 may be included in the comparison, though not directly. The compounds dealt with therein were less soluble in water, and solvents containing 20—25% of methyl alcohol had to be used. Trials with *ON*-dimethylnitramine (Table 4) showed that this change reduced the rate by about 20%; conversely, we believe that if the catalytic constants of Table 2 are increased by one-quarter, the resultant figures compare reasonably with those in Table 1.

In Table 3 variations of the catalytic constant are set out in ratio form. It is obvious

[3] Ingold, "Structure and Mechanism in Organic Chemistry" Bell and Sons, London, 1953, Chapter XIV.

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TABLE 1. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M *in hydrochloric acid, at* 45°.

Run no.	Compound	Acid (mole l.$^{-1}$ at 20°)	Method of measurement	First-order rate coeff., 10^3k (min.$^{-1}$)	Catalytic constant, k_{H^+} (l. mole^{-1} min.$^{-1}$)
1	Me·N:NO·OMe	0·520	U.V.	25·0	0·048
2	,,	0·493	Gas	23·3	0·047
3	,,	0·300	Gas	16·4	0·055
4	,,	0·0250	U.V.	1·35	0·054
5	Me·N:NO·OEt	0·500	Gas	22·1	0·044
6	,,	0·300	Gas	12·9	0·043
7	,,	0·100	Gas	4·4	0·044
8	Me·N:NO·OPr^i	0·500	Gas	18·8	0·038 *
9	,,	0·300	Gas	11·4	0·038 *
10	Et·N:NO·OMe	0·101	Gas	40·5	0·40
11	,,	0·0500	Gas	20·4	0·41
12	,,	0·0250	Gas	9·9	0·40
13	Et·N:NO·OEt	0·1007	Gas	37·8	0·38
14	,,	0·0250	Gas	10·4	0·42
15	Et·N:NO·OPr^i	0·1007	Gas	29·0	0·29
16	,,	0·0500	Gas	14·3	0·29
—	Pr^{i}N:NO·OMe	(From Part IX, *J.*, 1955, 3997)		—	3·6
17	Pr^{i}N:NO·OEt	0·0250	U.V.	79·0	3·2
18	,,	0·0050	U.V.	16·5	3·3
19	,,	0·0050	Gas	16·0	3·2

* In this case only there is some discrepancy between the " gas " and " U.V." measurements: interpolation from U.V. results at 35°, 40°, and 50° (Table 4) gives 0·044 for this rate.

TABLE 2. *Decomposition of* ON-*dialkylnitramines, initially* 0·05M *in hydrochloric acid containing methanol, at* 45°.

Run no.	Compound	Acid (mole l.$^{-1}$ at 20°)	Method of measurement	First-order rate coeff., 10^3k (min.$^{-1}$)	Catalytic constant, k_{H^+} (l. mole^{-1} min.$^{-1}$)
20	Pr^i·N:NO·OPr^i	0·0250 (*a*)	U.V.	39·1	1·57
21	,,	0·0050 (*a*)	U.V.	7·9	1·59
22	,,	0·0050 (*a*)	Gas	8·2	1·65
23	Bu^t·N:NO·OMe	$6·85 \times 10^{-5}$ (*b*)	U.V.	23·5	291 (*c*)
24	,,	$9·0 \times 10^{-5}$ (*b*)	U.V.	30·0	294 (*c*)
25	,,	$10·5 \times 10^{-5}$ (*b*)	U.V.	33·0	281 (*c*)
26	,,	$20·0 \times 10^{-5}$ (*b*)	U.V.	63·5	301 (*c*)
27	,,	$50·1 \times 10^{-5}$ (*b*)	U.V.	154·0	303 (*c*)
56	,,	$18·6 \times 10^{-5}$ (*b*)	U.V.	64·3	328 (*c*)
57	,,	$18·6 \times 10^{-5}$ (*b*)	U.V.	62·1	317 (*c*)
28	$C_5H_{11}^{neo}$·N:NO·OMe	0·100 (*a*)	U.V.	51·0	0·51
29	,,	0·050 (*a*)	U.V.	26·3	0·53
30	,,	0·025 (*a*)	U.V.	13·2	0·53

(*a*) Methanol, 25% v/v. (*b*) Methanol, 20% v/v. The acid concentration was determined by means of a pH meter. (*c*) *N-tert.*-Butyl-*O*-methylnitramine shows catalysis by water at 45°: the " spontaneous " rate (10^3k, 3·7 min.$^{-1}$ at 45°, see footnote, Table 4) has been deducted before calculation of the catalytic constant.

TABLE 3. *Values of the catalytic constant* k_{H^+} *for the decomposition of compounds* R·N:NO·OR′ *in water at* 45°, *set out as ratios.*

For changes in R, with R′ constant				For changes in R′, with R constant			
Nature of R	Nature of R′			Nature of R′	Nature of R		
	(1) Me	(2) Et	(3) Pr^i		(4) Me	(5) Et	(6) Pr^i
Me	1·0	1·0	1·0	Me	1·0	1·0	1·0
Et	8	9	7·5	Et	$0·8_5$	1·0	0·9
Pr^i	71	73	50 †	Pr^i	$0·7_5$	0·7	0·6 †
Bu^t	7000 †	—	—				
$C_5H_{11}^{neo}$	13 †	—	—				

* Size of unit in each vertical column: 1, 0·051; 2, 0·044; 3, 0·038; 4, 0·051; 5, 0·40; 6, 3·6 l. mole^{-1} min.$^{-1}$.

† Approx. values, based on 5/4 times observed rate in the presence of methanol.

that the rates of decomposition are connected with the ability of the group R (in R·N:NO·OR′) to release electrons by the inductive mechanism: the rates lie in the theoretical order Me < Et < $Pr^i \ll Bu^t$, and *neo*-C_5H_{11} falls in the expected position between ethyl and *iso*propyl. In this, the reaction resembles the hydrolysis of alkyl bromides in moist formic acid, investigated by Hughes and his colleagues;[4] quantitatively, ethyl appears to be more, and *tert.*-butyl less, effective in the nitramine decomposition than in the bromide hydrolysis. As in the bromide hydrolysis, the rate for *neo*pentyl is comparable with that for ethyl; but in the nitramine decomposition the *neo*pentyl group appears to be the more effective. Dostrovsky and Hughes[4] considered that their values might still contain some contribution from a bimolecular mechanism of hydrolysis; and we suggest that the rate sequence for the *ON*-dialkylnitramine decomposition follows the theoretical one, for the inductive effect in a unimolecular mechanism, fully as well as in any other reaction previously investigated.

It thus seems safe to assume that the ease of fission of the *N*-alkyl bond plays a major part in the mechanism of decomposition. Changes in R′ have a comparatively small effect, in the opposite sense to changes in R. We regret that an attempt to prepare an *O-tert.*-butyl compound was unsuccessful.

Some measurements have been made of the parameters A and E in the kinetic equation $k = A \exp(-E/RT)$. Good linear plots were obtained, in the range 25—50°, of log k_{H^+} against $1/T$(°K), and the results are given in Table 4. Comparison of the second and the last line of the Table shows that a change in the activation energy has been the main factor in determining the change in rate: the observed change in A acts in the opposite sense. The more rapid decomposition of Pr^iN:NO·OMe (line d) compared with Me·N:NO·OMe (line a) seems to be due partly to a fall in E, and partly to a rise in A; the values of the parameter A are reasonable, but inconclusive. If we write A in the form PZ, and take[5] the collision frequency Z to be 3×10^{11} l. mole^{-1} sec.$^{-1}$, then the values of the probability factor P range from 0·3 to 20: these slightly favour a unimolecular mechanism, since in only one case is P less than unity.[6]

TABLE 4. *The parameters A and E in the kinetic equation* $k = A \exp(-E/RT)$.

Run nos., solvent, and notes	Compound (initially 0·05M)	Mean values of k_{H^+} (or k_{h_0} if applicable) in l. mole^{-1} min.$^{-1}$, measured by the U.V. technique at temperatures of 25°	35°	40°	45°	50°	$\log_{10} A$ (l. mole^{-1} sec.$^{-1}$)	E (kcal. mole^{-1})
a	Me·N:NO·OMe	0·0053	0·0178	0·0305	0·051	0·093	11·6	21·3
b	Me·N:NO·OMe	—	0·013	0·023	0·041	0·076	12·6	23·0
c	Me·N:NO·OPr^i	—	0·0153	0·0255	—	0·077	11·6	21·4
d	Pr^i·N:NO·OMe	0·38	1·29	2·13	3·60	5·95	12·8	20·4
e	Bu^t·N:NO·OMe	66	150	—	323	—	11·0	15·0

Run nos. are grouped in order of increasing temperature. a: 58; 31, 32; 33, 34; 1–4; 35, 36; in HCl–H_2O. b: 37; 38; 39; 40; in HCl–H_2O–MeOH, H_2O–MeOH 80/20, v/v. c: 41, 42; 43, 44; 45, 46; in HCl–H_2O. d: 25° and 45°, *loc. cit.*[1]; remaining temp., 47, 48; 49; 50, 51; in HCl–H_2O. e: 52, 53; 54, 55; 56, 57; all in the same solvent (HCl–H_2O–MeOH, H_2O–MeOH 80/20, v/v) of [H^+] $1·86 \times 10^{-4}$ mole l.$^{-1}$ at 25°, to avoid errors in E which might be introduced by the measurement of various pH values; and after making allowance for water catalysis. Water-catalysis gave the following rates in 0·015M-sodium hydroxide solution: 10^3k 3·7, 1·0, and 0·2 min.$^{-1}$ at, respectively, 45°, 35°, and 25°.

Reference has already been made, on several occasions in this paper, to the catalytic constant k_{h_0} as an alternative to k_{H^+}. In dilute acid, when the Hammett acidity function H_0 is equal to pH, k_{h_0} is identical with k_{H^+}. In more concentrated acid, the rate of a unimolecular acid-catalysed reaction is dependent upon the acidity function, whilst the rate of a bimolecular reaction involving a molecule of water depends on the stoicheiometric

[4] Bateman and Hughes, *J.*, 1940, 945; Dostrovsky and Hughes, *J.*, 1946, 171.
[5] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 115.
[6] Hinshelwood and Winkler, *J.*, 1936, 376.

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concentration of hydrogen ion.[7] Application of this test to *ON*-dimethylnitramine (Table 5) showed that water is not covalently involved in the rate-determining stage of the decomposition: graphically the plot of $\log_{10}k$ against H_0 is linear, with unit slope, whilst that against pH is curved. A similar conclusion can be drawn for *N-iso*propylnitramine, though with less certainty, from the results reported in Table 6: in this case the best line in the plot of $\log_{10}k$ against H_0 has a slope of 0·94, whilst the values from runs 64, 65, and 66 are precisely linear, with a slope of 0·91.

TABLE 5. *Decomposition of* ON-*dimethylnitramine, initially* 0·05M *in hydrochloric acid, at* 25°.

Run no.	$[H^+]$ (mole l.$^{-1}$ at 25°)	h_0 at 25°	10^3k_1 (min.$^{-1}$)	$10^3k_{H^+}$ (l. mole^{-1} min.$^{-1}$)	$10^3k_{h_0}$ (l. mole^{-1} min.$^{-1}$)
58	1·01	1·15	6·1	5·9	5·3
59	2·25	4·17	22·5	10	5·4
60	3·01	8·22	46	15	5·6
61	4·07	19·05	104	26	5·5
62	5·01	41·70	256	51	6·0

All measurements were made by the U.V. method. The h_0 figures are derived from published values [8] of H_0.

TABLE 6. *Decomposition of* N-iso*propylnitramine, initially* 0·05M *in hydrochloric acid, at* 45°.

Run no.	$[H^+]$ (mole l.$^{-1}$ at 25°)	h_0 at 25°	10^3k_1 (min.$^{-1}$)	$10^3k_{H^+}$ (l. mole^{-1} min.$^{-1}$)	$10^3k_{h_0}$ (l. mole^{-1} min.$^{-1}$)
63	0·77	0·89	0·75	0·97	0·84
64	2·20	4·1	3·3	1·5	0·80
65	3·10	7·9	6·0	1·9	0·76
66	4·40	25·1	13·3	3·0	0·53

All measurements were made by the manometric method. The h_0 figures are derived from published values [8] of H_0.

DISCUSSION

It was recognised by early workers that the acid-catalysed decomposition of nitramines was linked with the occurrence of the " iso " structure (·N:NO·O·), either as such in the molecule (*e.g.*, *ON*-dialkylnitramines, R·N:NO·OR′), or as a possible tautomer (*e.g.*, primary nitramines, $R{\cdot}NH{\cdot}NO_2 \rightleftharpoons R{\cdot}N{:}NO{\cdot}OH$). Of the other groups of aliphatic *N*-nitro-compounds at present known, two—the secondary nitramines [$(Alkyl)_2N{\cdot}NO_2$] and the secondary nitramides [(Alkyl)(Acyl)N·NO_2]—cannot give rise to " iso " structures, and are remarkably stable in acid media.[9] The remaining group—the primary nitramides (Acyl·NH·NO_2)—can give rise to " iso " structures, and are in fact irreversibly decomposed by acid, though relatively slowly. The kinetics of this reaction have not been investigated in detail, but, at least in the case of nitroguanidine,[10] the products have been successfully predicted by analogy with the acid-catalysed decomposition of primary nitramines: salts of nitroguanidine [*e.g.*, $NO_2{\cdot}NH{\cdot}C(NH_2)_2{}^+X^-$] were classified as primary nitramides, since the amidinium portion $C(NH_2)_2{}^+$ could be regarded as acylic in character.[10]

For those groups which are relatively stable in acids—in particular the nitramides, both primary and secondary—the position is complicated by denitration as an alternative mode of decomposition. In suitable solvents (60% $HClO_4$, 80—100% H_2SO_4) equilibrium is established between nitration and denitration.[11] In general, primary nitramides are more rapidly decomposed by the denitration reaction than by the irreversible decomposition

[7] Ingold, *op. cit.* (ref. 3), p. 772; Hawke and Stimson, *J.*, 1956, 4676, give a number of recent references.

[8] Bell, Dowding, and Noble, *J.*, 1955, 3106.

[9] Holstead and Lamberton, *J.*, 1952, 1886.

[10] *Idem*, *J.*, 1954, 2391.

[11] Simkins and Williams, *J.*, 1952, 3086; 1953, 1386; Holstead, Lamberton, and Wyatt, *J.*, 1953, 3341; Holstead and Lamberton, *J.*, 1953, 3349; Hardy-Klein, *J.*, 1957, 70.

with which we are here concerned; but the irreversible decomposition is distinct in that it gives different products and, in particular, results in the loss of nitrogen from the system in the form of nitrous oxide.

In this, and earlier papers (refs. 1, 2, 12, 13) it has been shown that the acid-catalysed irreversible decomposition of the structure R·N:NO·OR′ (R = alkyl, R′ = alkyl or H) (*a*) involves scission of the molecule at the R–N and N–OR′ bonds, (*b*) gives rise to the ion R^+, (*c*) is favoured by electron-donation from R, and (*d*) proceeds at a rate directly proportional to the ability of the solvent and solute molecules, taken as a whole, to furnish protons to the molecule which will undergo decomposition.

These results suggest a mechanism of decomposition analogous to the mode of acid hydrolysis of esters which Ingold [3] designates as $A_{AC}1$, but with an additional shift of electrons leading to the liberation of the cation R^+ (equations 1 and 2).

$$\text{(1)}\quad \text{R·N:NO·OR}' + \text{H}^+ \overset{\text{Fast}}{\rightleftharpoons} \text{R·N:NO·}\overset{+}{\text{O}}\text{HR}'$$

$$\text{(2)}\quad \text{R—}\overset{\curvearrowright}{\text{N}}\text{:NO—}\overset{+}{\text{O}}\text{HR}' \xrightarrow{\text{Slow}} \text{R}^+ + \text{N}_2\text{O} + \text{R}'\text{OH}$$

The Arrhenius parameters are at least consonant with this mechanism. The dispersion of charge, in the transition state of (2), should produce a slight increase of rate on reducing the polarity of the solvent.[14] We find in fact a slight decrease : this may well be due to an alteration in equilibrium (1)—*i.e.*, to a less efficient catalysis, by a given quantity of acid, in the less polar medium.

For simplicity, we prefer to present the bond scissions as concurrent parts of a single mechanistic stage. The scissions may, however, be successive; in this case the protonated complex would break down according to equations (3) and (4), or (5) and (6).

$$\text{(3)}\quad \text{R·N:NO·}\overset{+}{\text{O}}\text{HR}' \xrightarrow{\text{Slow}} \text{R·N:}\overset{+}{\text{N}}\text{O} + \text{R}'\text{OH}$$

$$\text{(4)}\quad \text{R·N:}\overset{+}{\text{N}}\text{O} \xrightarrow{\text{Fast}} \text{R}^+ + \text{N}_2\text{O}$$

$$\text{(5)}\quad \text{R·N:NO·}\overset{+}{\text{O}}\text{HR}' \xrightarrow{\text{Slow}} \text{R}^+ + \bar{\text{N}}\text{:NO·}\overset{+}{\text{O}}\text{HR}'$$

$$\text{(6)}\quad \bar{\text{N}}\text{:NO·}\overset{+}{\text{O}}\text{HR}' \xrightarrow{\text{Fast}} \text{N}_2\text{O} + \text{R}'\text{OH}$$

Both R and R′ have an influence upon the rate of decomposition, and though the evidence is weaker for R′ than for R, it certainly rules out reaction (6), and probably reaction (4), as rate-determining stages: (4) and (6), if they occur at all, must be fast with respect to (3) and (5). It should be added that, in principle, reactions (3) and (5) could be treated as rapidly established equilibria, and variations in R and R′ could exert their effect by changing the position of equilibrium. If this were so, reactions (4) and (6) could be rate-determining; but we suggest that this treatment is inadmissible in the context of the actual conditions of the decomposition. In (3) there would seem to be no good reason to postulate the reaction of $\text{R·N:}\overset{+}{\text{N}}\text{O}$ exclusively with R′OH rather than with water molecules, which are at least a thousand times more numerous; and any reaction with water molecules would remove $\text{R·N:}\overset{+}{\text{N}}\text{O}$ to produce the relatively stable primary nitramine R·NH·NO_2—which is not observed. Similarly, (5) could not be formulated as an equilibrium, since R^+ would be removed by reaction with water, or olefin formation: decomposing solutions would contain $\bar{\text{N}}\text{:NO·}\overset{+}{\text{O}}\text{HR}'$ (or a tautomer thereof), and the ultraviolet absorption spectrum would be changed. Quite generally, the agreement between the spectroscopic and the manometric method of analysis suggests the first bond-scission to

[12] Barrott, Denton, and Lamberton, *J.*, 1953, 1998.
[13] Denton and Lamberton, *J.*, 1955, 1655.
[14] Ingold, *op. cit.* (ref. 3), p. 347.

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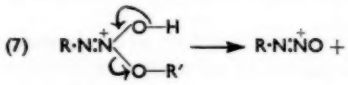
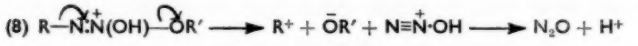
be rate-determining; and whilst we do not deny that (3) and (5)—if they occur at all—are in theory reversible, we consider that the extent of any reverse reaction cannot be of significance.

We would formulate the acid-catalysed decomposition of primary nitramines in similar terms (*viz.*, equations 1 and 2, R = alkyl, R′ = H). The observed rate of decomposition will here depend, not only on the stability of the structure R·N:NO·OH, but also on the position of the tautomeric equilibrium $R{\cdot}NH{\cdot}NO_2 \rightleftharpoons R{\cdot}N{:}NO{\cdot}OH$, which is probably very largely to the left. Variations in the position of equilibrium, with variable R, may well account for the incomplete correlation, in the primary nitramine series, of electron-donation by R with the observed rate of decomposition.[12,13]

Site of Initial Protonation.—Our choice (equation 1) was made on grounds of analogy with ester hydrolysis, and since this position of protonation leads most simply to the known products of the reaction; but alternative structures of the protonated complex are conceivable. We exclude $R{\cdot}NH_2{\cdot}NO_2$ and R·NH·NO·OH, since these are not consistent with the stability of structures such as $R_2N{\cdot}NO_2$; and for this reason we now feel that the step $R{\cdot}NH{\cdot}NO_2 + H^+ \longrightarrow R^+ + H_2N{\cdot}NO_2$, suggested in an earlier paper,[12] is unlikely. The complex R·NH:NO·OR′ could initiate a decomposition analogous to equation (5), but would provide no immediate reason for the fission of the N–OR′ bond; R·N:N(OH)·OR′ could initiate processes such as (7) or (8):

(7) 

(8) 

It is clear that the presence (or absence) of nitramine ($H_2N{\cdot}NO_2$) as an intermediate would be to some extent diagnostic. Though Davis and Blanchard[15] reported the isolation, under certain conditions, of nitramine from nitrourea, we still regard this as an open question: we have been unable, as yet, to find any sign of nitramine in decomposing solutions of primary nitramines; methylenedinitramine[16] is exceptional, and a special case. To sum up: we do not imply that these alternative protonations are impossible, but merely that they seem, on the basis of our present knowledge, to be less relevant to the process of irreversible decomposition.

Experimental

Reaction rates were evaluated on the basis of natural logarithms, and temperatures were controlled to within one-tenth of a degree. Acid concentrations have been corrected on the assumption that the solutions showed the same expansion as water over the range 20—50°; but, in the absence of suitable data, the h_0 values used [8] relate to 25°. The methods of measurement by the manometric [12] and spectroscopic [1] techniques have been previously described.

All compounds reported as *ON*-dialkylnitramines gave an immediate evolution of gas on treatment with 40% sulphuric acid at room temperature. *NN*-Dialkylnitramines can readily be freed from traces of their *ON*-isomerides by treatment with 40% sulphuric acid, but no method, other than repeated distillation, is yet known for the purification of the *ON*-dialkylnitramines. All the *ON*-dialkylnitramines used for kinetic observations were distilled at least twice or thrice. Even so, the residual ultraviolet absorption after decomposition indicated, in a few cases, the presence of traces of the stable *NN*-isomeride; quantitatively, the proportion of the *NN*-isomeride was never greater than 5%. Since the reaction kinetics, in a given medium, are of the first order, the results obtained manometrically are unaffected by traces of the stable

[15] Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.
[16] Lamberton, Lindley, and Speakman, *J.*, 1949, 1650.

isomeride. In the determination of rates by the spectroscopic method allowance was made, whenever necessary, for the (constant) absorption produced by traces of the *NN*-isomeride.

The silver salts employed in alkylation were precipitated from water by the action of a slight excess of silver nitrate on the *iso*propylammonium or *cyclo*hexylammonium salts of the primary nitramines: they were collected, washed successively with water, acetone, and ether, and " dried " *in vacuo*. The nitramines themselves were prepared by standard methods;[12,13,14] the following salts appear to be new: cyclo*hexylammonium methylnitramine*, needles, m. p. 130—131° from ethanol–chloroform (Found: C, 47·9; H, 9·7. $C_7H_{17}O_2N_3$ requires C, 48·0; H, 9·7%); *cyclo*hexylammonium *tert.*-butylnitramine, microcrystalline, m. p. 125—126°; iso*propylammonium* neo*pentylnitramine*, nacreous plates, m. p. 128°, from ethanol–ether (Found: C, 50·0; H, 10·8; N, 21·6. $C_8H_{21}O_2N_3$ requires C, 50·2; H, 11·0; N, 22·0%).

O-*Alkyl*-N-*methylnitramines*.—The *O*-methyl and *O-iso*propyl compounds have recently been described.[1] The *O*-ethyl compound, prepared by the same general method, had b. p. 40—42°/20 mm. (Found: C, 34·3; H, 7·6. Calc. for $C_3H_8O_2N_2$: C, 34·6; H, 7·7%): Franchimont and Umbgrove [18] reported b. p. 35°/16 mm. Refluxing a suspension of the silver salt of methylnitramine (7 g.) in ether (75 ml.) and *sec.*-butyl bromide (10 g.) for 12 hr. yielded, after removal of silver bromide and subsequent fractional distillation, (±)-O-sec.-*butyl*-N-*methylnitramine* (2 g.), b. p. 73—75°/40 mm. (Found: C, 45·2; H, 9·1. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

O-*Alkyl*-N-*ethylnitramines*.—The following were prepared by the same general method (above, and ref. 1): *N*-ethyl-*O*-methylnitramine, b. p. 52—53°/40 mm. (Found: C, 34·8; H, 7·8. Calc. for $C_3H_8O_2N_2$: C, 34·6; H, 7·7%) (Franchimont and Umbgrove [18] gave b. p. 36—38°/20 mm.): *ON*-diethylnitramine, b. p. 45—47°/18 mm. (Found: C, 40·7; H, 8·7. Calc. for $C_4H_{10}O_2N_2$: C, 40·7; H, 8·5%) (Franchimont and Umbgrove [18] gave b. p. 46—50°/18 mm): N-*ethyl*-O-iso*propylnitramine*, b. p. 50—54°/18 mm. (Found: C, 45·8; H, 9·2. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

O-*Alkyl*-N-iso*propylnitramines*.—The *O*-methyl and *O-iso*propyl compounds have recently been described.[1] O-*Ethyl*-N-iso*propylnitramine*, prepared in the same manner, had b. p. 64—65°/30 mm. (Found: C, 45·8; H, 9·2. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

N-tert.-*Butyl*-O-*methylnitramine*.—The silver salt of *tert.*-butylnitramine (11 g.) was set aside at room temperature for 10 days with methyl iodide (10 ml.) in ether (125 ml.), and the mixture thereafter refluxed for 4 hr. Removal of silver iodide, and subsequent fractional distillation, yielded N-tert.-*butyl*-O-*methylnitramine*, b. p. 59—61°/35 mm. (Found: C, 45·8; H, 8·8. $C_5H_{12}O_2N_2$ requires C, 45·5; H, 9·1%).

Miscellaneous Compounds, and an Unsuccessful Preparation.—*O*-Methyl-*N-neo*pentylnitramine has recently been described.[1] The *O*- and *N*-methyl derivatives of *N-cyclo*hexylnitramine have been prepared, but not examined kinetically. The *cyclo*hexylammonium salt [17] of *cyclo*hexylnitramine was converted into the silver salt, and alkylated to yield N-cyclo*hexyl-O-methylnitramine*, b. p. 100—101°/17 mm. (Found: C, 53·2; H, 8·9; N, 17·3. $C_7H_{14}O_2N_2$ requires C, 53·2; H, 8·9; N, 17·7%). *N*-Methyl*cyclo*hexylamine hydrochloride was nitrated, by the method of Kingdon and Wright,[19] to yield N-cyclo*hexyl*-N-*methylnitramine*, b. p. 88—89°/0· mm. (Found: C, 53·5; H, 9·0; N, 17·6%). An attempt to prepare *O-tert.*-butyl-*N*-methylnitramine was unsuccessful: on addition of *tert.*-butyl iodide (15 g.) to the silver salt of methylnitramine (8·5 g.) in ether (100 ml.) a vigorous reaction occurred; gaseous products were evolved, and the ether boiled. The mixture was cooled, and thereafter kept in the dark for 4 days. On working up in the usual manner (but with a thiosulphate wash to remove iodine) no isolable product was obtained.

Evidence against the Formation of Methylnitramine during the Decomposition of N-*Methyl*-O-iso*propylnitramine*.—A solution of *N*-methyl-*O-iso*propylnitramine (0·2508 g.) in 0·1M-hydrochloric acid (50 ml.) was kept at 45°, and samples (5 ml.) were withdrawn at once, and after time intervals known to correspond to 10, 20, 30, 40, 50, 60, 75, and 100% decomposition. All the samples had a titre of 9·4 ± 0·05 ml. of 0·0502M-sodium hydroxide. Methylnitramine did not undergo any decomposition in similar conditions of time (24 hr.), temperature, and acidity: a 1% yield of methylnitramine would have raised the sodium hydroxide titre by 0·042 ml.

[17] Curry and Mason, *J. Amer. Chem. Soc.*, 1951, **73**, 5042.
[18] Franchimont and Umbgrove, *Rec. Trav. chim.*, 1897, **16**, 359.
[19] Kingdon and Wright, *J. Amer. Chem. Soc.*, 1950, **72**, 1030.

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The Reaction-cycle (+)-sec.-*Butyl Alcohol* ⟶ (−)-sec.-*Butyl Bromide* ⟶ (+)-O-sec.-*Butyl*-N-*methylnitramine* ⟶ (+)-sec.-*Butyl Alcohol*.—Optically active *sec.*-butyl alcohol ($[\alpha]_D^{23}$ +12·3°; 89·5% optically pure), prepared *via* the brucine hydrogen phthalate,[20] was converted into *sec.*-butyl bromide by Letsinger's [21] modification of the method of Levene and Marker.[22] The product had $[\alpha]_D^{21}$ −17·3°. The reaction is known to occur with reversal of configuration and considerable racemisation: on the basis of Letsinger's [21] largest (calculated) value (−26·1°) for the (−)-bromide, our product was of *not more* than 66% optical purity. This was used to alkylate the silver salt of methylnitramine, and yielded an active sample of *O-sec.*-butyl-*N*-methylnitramine, $[\alpha]_D^{21}$ +11·1°, d_4^{21} 0·978 (Found: C, 45·3; H, 9·0%. For preparation and required values, see under *O*-alkyl-*N*-methylnitramines, p. 4205). By analogy with the work of Kornblum [23] on the alkylation of silver nitrite, the nitramine is probably formed with reversal of configuration, and very little racemisation: if so, pure (+)-*O-sec.*-butyl-*N*-methylnitramine would have $[\alpha]_D^{21}$ at least +17°. This estimate is not essential for our argument.

Active samples of *O-sec.*-butyl-*N*-methylnitramine were heated in sealed Pyrex tubes with acidified aqueous methanol until decomposition was complete, as indicated by constancy of optical rotation. Active *sec.*-butyl alcohol was unaffected by the same treatment. Duplicate experiments were carried out, with consistent results, and details are given of one set. A solution of *O-sec.*-butyl-*N*-methylnitramine [65·4 mg. made up to 1·27 ml. with methanol–water (60/40, v/v, 0·5M in hydrochloric acid); *c* 5·15%] had α_D^{21} (100 mm.) + 0·64°, $[\alpha]_D^{21}$ +12·4°. After 60 hr. at 60° (thermostat), the observed rotation, α_D^{21} (100 mm.), had fallen to +0·21°, unchanged by a further 30 hours' heating. Quantitative liberation of the alcohol from 65·4 mg. of the *O-sec.*-butylnitramine would yield 36·7 mg. of *sec.*-butyl alcohol: hence the concentration of *sec.*-butyl alcohol in the spent solution is not more than 2·89%, and $[\alpha]_D^{21}$ not less than +7·3°. A sample of the initial butyl alcohol, at comparable concentration in the same solvent, showed a negligible change (α_D^{21} +0·37° ⟶ +0·36°) on 70 hours' heating at 60°; the mean value gives $[\alpha]_D^{21}$ +13·0° (*c* 2·81). The alcohol produced from the nitramine cannot therefore be less than 7·3 × 100/(13·0 × 100/89·5) = 50% optically pure, and was derived from a bromide which could not have been more than 66% optically pure: the retention of activity through the whole series alcohol ⟶ bromide ⟶ nitramine ⟶ alcohol is not less than 7·3 × 100/13·0 = 56%.

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[20] Pickard and Kenyon, *J.*, 1911, **45**; Ingersoll, "Organic Reactions," Vol. II, Wiley and Sons, New York, 1944, p. 403; Stevens, Morrow, and Lawson, *J. Amer. Chem. Soc.*, 1955, **77**, 2341.
[21] Letsinger, *J. Amer. Chem. Soc.*, 1948, **70**, 406.
[22] Levene and Marker, *J. Biol. Chem.*, 1931, **91**, 412.
[23] Kornblum, *J. Amer. Chem. Soc.*, 1955, **77**, 6261, 6269.

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843. *Cobalt Phosphates. Part I. The Orthophosphate Group as Ligand in Some Cobalt(III) Ammine Complexes.*

By Salha S. Daniel and J. E. Salmon.

Attempts to prepare phosphatopentamminocobalt(III) complex salts by various methods all yielded aquopentamminocobalt(III) phosphates, whilst every attempt to obtain a phosphato-complex from triamminocobalt(III) complexes gave cobalt(II) compounds.

Only in the tetrammine series were two compounds with the properties expected for phosphato-complexes obtained. The first, $[Co(NH_3)_4PO_4],2H_2O$, had properties quite distinct from those of the isomer $[Co(NH_3)_4(H_2O)_2]PO_4$ which was also prepared. The second appeared to be $[Co(NH_3)_4HPO_4]_3PO_4$, but its constitution could not be established with certainty. The properties of the neutral complex indicated that in it the phosphate is a chelate group.

Although several hexammino-, aquopentammino-, and diaquotetrammino-cobalt(III) orthophosphates are known,[1] few cobalt(III) complexes containing a phosphato-group as ligand have been described. Duff [2] reported the preparation of the complex compounds $[Co(NH_3)_5PO_4],2H_2O$ and $[Co(NH_3)_5HPO_4]H_2PO_4,2H_2O$, and Duval and Duval [3] described an anhydrous compound $[Co(NH_3)_5PO_4]$, but only one phosphatotetrammino-complex $[Co(NH_3)_4PO_4],nH_2O$ ($n = 2$ or 3) appears to have been reported.[4]

The preparation of the hydrated phosphatopentamminocobalt(III) compound described by Duff was disputed by Klement,[4] and that of the corresponding anhydrous compound [3] is not described in sufficient detail for the method to be repeated. The neutral phosphatotetrammino-complex was not prepared directly, but was isolated from the complex products—containing both cobalt(II) and cobalt(III) compounds—of the reaction between sodium phosphate and either dichlorodiaquodiammino- or dichloroaquotriamminocobalt(III) compounds.[4]

There was, therefore, little evidence relating to the direct introduction of the phosphato-group into cobalt(III) ammine complexes. Less was known of the properties of the phosphato-groups as a ligand in such complexes than of those of the carbonato- or sulphato-groups, which can apparently occupy either one or two co-ordination positions.[5] We have therefore studied the preparation of phosphatocobalt(III) ammine complexes and their properties.

Experimental and Results

Starting Materials.—The following compounds used in attempts to prepare phosphatocobalt(III) complexes were prepared by methods given in the references: $[Co(NH_3)_5Cl]Cl_2$,[6] $[Co(NH_3)_5H_2O]Cl_3$,[7] $[Co(NH_3)_5CO_3]NO_3$,[8] $[Co(NH_3)_5NO_3](NO_3)_2$,[9] $[Co(NH_3)_4CO_3]NO_3$,[10] *cis*-$[Co(NH_3)_4(H_2O)Cl]SO_4$,[11] $[Co(NH_3)_4(H_2O)_2]Cl_3$,[10] $[Co(NH_3)_3(H_2O)_3]Cl_3$,[12] and $[Co(NH_3)_3(NO_2)_3]$.[13] In every case the product was completely analysed. Apart from the carbonatopentamminocobalt(III) nitrate, which appeared to contain a little of the tetrammino-salt, all were pure. The " aquo-complexes " were prepared immediately before use.

[1] Mellor, " Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London, 1935, Vol. XIV, p. 856.
[2] Duff, *J.*, 1923, **123**, 560.
[3] Duval and Duval, *Compt. rend.*, 1929, **189**, 537.
[4] Klement, *Z. anorg. Chem.*, 1926, **156**, 237.
[5] Martell and Calvin, " Chemistry of the Metal Chelate Compounds," Prentice Hall, New York, 1952, p. 134.
[6] King, " Inorganic Preparations," George Allen and Unwin, London, 1950 (revised edn.), p. 106.
[7] Ref. (6), p. 109.
[8] Werner and Goslings, *Ber.*, 1903, **36**, 2378.
[9] Palmer, " Experimental Inorganic Chemistry," Cambridge Univ. Press, Cambridge, 1954, p. 535.
[10] Ref. (6), p. 110.
[11] Ref. (9), p. 545.
[12] Ref. (6), p. 111.
[13] Ref. (9), p. 539.

Analytical Methods.—The following methods were used for both starting materials and products: (a) *Chloride.* Gravimetrically as silver chloride. (b) *Ammonia.* By evolution and absorption in excess of standard acid. (c) *Nitrite* (*nitro-groups*) *and* (d) *nitrite.* By evolution as ammonia after reduction with Devarda's alloy. (e) *Total phosphate.* Gravimetrically as ammonium phosphomolybdate. (f) *Ionisable phosphate.* Gravimetrically by precipitation as silver phosphate from cold aqueous solution. (g) *Cobalt.* The complex was decomposed by boiling with a slight excess of sodium hydroxide solution; the precipitate thus formed was dissolved by addition of the minimum quantity of dilute hydrochloric acid and warming; 50 ml. (*i.e.*, excess) of a standard solution (approx. M/100) of disodium ethylenediaminetetra-acetate were added, and the solution neutralised with ammonia, boiled for 2 min., and cooled; 2 or 3 drops of 2N-ammonia were then added, and the excess of edta was determined by titration with standard (*ca.* M/100) zinc sulphate solution, with Eriochrome Black-T as indicator; the presence of phosphate in the amounts occurring in our samples did not interfere. (h) *Carbonate and* (j) *water.* Both determined by difference.

Conductivity Measurements.—Because of the very low solubility in water of the compounds containing phosphate, measurements were made on their saturated solutions in conductivity water, and their concentrations were then obtained from a determination of cobalt content. Measurements were made on fresh solutions at 25° by use of a conventional conductivity cell with an A.C. Wheatstone bridge circuit. The molar conductances, shown in Table 1, were calculated on the assumption that the molecular weights were identical with the formula weights.

TABLE 1. *Molar conductances at* 25°.

Compound	Dilution (l. mole^{-1})	Molar conductance * (ohm^{-1} cm.^{2} mole^{-1})	No. of ions indicated
C	2564	409	4
D	2337	318	3—4
E	2033	47	0
F	1953	225	2—3

* Calculated on the assumption that the molecular weight is given by the formula weight.
† For key to letters, see details of preparations.

Absorption Spectra.—These were determined in the range 3000—8000 Å by use of apparatus of commercial design. Solutions of approximately M/100-concentration were of suitable optical density for use with 1 cm. cells. Those of compounds containing phosphate were obtained by use of M/100-phosphoric acid as solvent; those of the other compounds used as reference substances were aqueous solutions. All measurements were made on fresh solutions. The extinction coefficients given in Table 2 were calculated on the assumption that the molecular weights were given by the formula weights.

TABLE 2. *Absorption spectra for visible and ultraviolet regions.*

Values of $\lambda_{max.}$ (Å) and $\varepsilon_{max.}$

Compound	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
D *	3420	43	4850	48	—	—
$[Co(NH_3)_5(H_2O)]Cl_3$ †	3450	47	4940	48	—	—
$[Co(NH_3)_5Cl]Cl_2$ †	3570	43	5300	42	—	—
C *	3620	46	5100	54	—	—
E *	3650	23	5220	37	6950	61
F *	3520	38	5100	50	—	—
$[Co(NH_3)_4(H_2O)_2]Cl_3$ †	3560	38	5270	48	—	—
$[Co(NH_3)_4CO_3]NO_3$ †	‡	—	5260	57	7040	26

* Solvent, M/100-H_3PO_4. † Solvent, water. ‡ Strong peak at *ca.* 3500 Å.

Loss of Water from Products.—The loss in weight of samples of the compounds containing cobalt(III) and phosphate when heated to (*a*) 70°, (*b*) 90°, and (*c*) 110° was studied. At the conclusion of the experiments the samples were analysed for both cobalt and ammonia to ascertain the loss of ammonia, if any, and the loss of water was obtained by correction for this. The losses in water and ammonia from the various compounds when heated at three different temperatures are shown in Table 3. The rates at which compounds E and F lost weight when heated at 110° are given in Table 4.

Attempts to prepare Phosphate Complexes.—The various methods given below were tried.

Any solid products obtained were collected on a Büchner funnel and washed with either water or dilute aqueous ammonia (whichever had been used as solvent originally) to remove any unchanged starting material, then with alcohol or acetone. The product was then left to dry first in the air and, finally, for a short time in a desiccator ($CaCl_2$). All were very sparingly soluble in water, alcohol, or acetone, but dissolved readily in dilute solutions of mineral acids.

(1*a*) Duff's method " for salts derived from aquopentamminocobaltic nitrate." [1] Red crystals of the *aquopentammino-phosphate* (Compound A) were obtained {Found: Co, 21·29;

TABLE 3. *Loss of water from compounds on heating.*

	Loss of weight (%)						
			at 110° †			Calc. for loss of H_2O:	
Compound	at 70° * (total)	at 90° * (total)	(total)	(NH_3)	(H_2O)	of crystn.	total
A	1·43	—	6·98	2·79	4·19	6·55	13·10
B	—	—	7·23	2·86	4·37	6·55	13·10
C	—	—	16·29	12·97	3·32 §	0	0
D	3·14	3·36	11·07	2·09	8·98	12·30	18·45
E	14·03	16·47 ‡	20·35	6·81	13·54	13·96	13·96
F	0·45	1·27	12·74	2·25	10·49	0	13·96

* Samples heated to constant weight (5—7 days); no loss of ammonia except in case of compound E at 90°.
† Loss of weight after 15 days recorded.
‡ Loss due to ammonia, 2·58%.
§ Presumably due to some conversion of acid phosphate groups into pyrophosphate.

TABLE 4. *Rate of loss of weight at* 110°.

Time (hr.)		3	6	24	48	72	96	360
Wt. loss * (%) ...	E	19·96	20·02	20·19	20·30	20·34	20·35 †	20·35 †
	F	2·66	2·87	3·51	4·22	5·45	6·12	12·74

* Loss required for removal of $2H_2O$ = 13·96%.
† Loss required for removal of $2H_2O + 1NH_3$ = 20·56%.

NH_3, 31·02; PO_4 (total and ionisable), 34·35; H_2O, 13·34. $[Co(NH_3)_5H_2O]PO_4,H_2O$ requires Co, 21·43; NH_3, 30·97; PO_4 (total and ionisable), 34·53; H_2O, 13·10%}.

(1*b*) As method 1*a*, but applied to carbonatotetramminocobalt(III) nitrate. However, on the addition of nitric acid (initially) crystals of the diaquotetramminocabalt(III) nitrate separated.

(2*a*) Duff's method " for salts derived from carbonatopentamminocobaltic nitrate," [1] but, since in no case did concentration of the final solution yield a crop of crystals (even on standing), this solution was concentrated and then neutralised with dilute sodium hydroxide solution before addition of a solution (20 ml.) of $Na_2HPO_4,12H_2O$ (6·7 g.) and NaOH (0·75 g.); in an attempt to minimise any tendency for aquo-complexes to be formed, the temperature to which the solution containing the carbonato-complex and phosphoric acid was heated was changed from 60° (as in ref. 2) to 45°, but without any effect on the nature of the product; red crystals (Compound B) which were identical with those of Compound A were obtained.

(2*b*) Attempts to use method (2*a*) with carbonatotetramminocobalt(III) nitrate as starting material led to the precipitation of cobalt(III) oxide during the concentration of the acid solution; the method was modified as follows: 5 g. of the tetrammino-nitrate were heated with 30 ml. of 1M-phosphoric acid at 45°; when effervescence had ceased, the solution was cooled and excess of acid was neutralised with 2N-sodium hydroxide before the addition of a solution (20 ml.) of $Na_2HPO_4,12H_2O$ (6·7 g.) and NaOH (0·75 g.); violet crystals (3·5 g.) of the *Compound* C separated {Found: Co, 23·66; NH_3, 26·46; PO_4, 49·36 (total), 14·49 (ionisable); H_2O, 0·50. $[Co(NH_3)_4HPO_4]_3PO_4$ requires Co, 23·06; NH_3, 26·74; PO_4, 50·11 (total), 12·53 (ionisable); H_2O, 0%}.

(2*c*) As method (2*a*), but with triaquotriamminocobalt(III) chloride (5 g.) or trinitrotriamminocobalt(III) (5 g.) as starting material; it was necessary to avoid heating the acid solution otherwise the complex was decomposed; however, on neutralisation of the free acid present with sodium hydroxide, cobalt(II) ammonium phosphate separated.

(3*a*) To a solution obtained by warming to 60° 5 g. of either chloropentamminocobalt(III) chloride or nitratopentamminocobalt(III) nitrate with 100 ml. of 30% aqueous ammonia, a

second solution (25 ml.) containing 4·8 g. of $Na_2HPO_4,12H_2O$ and 0·5 g. of NaOH was added, and the mixed solution cooled; red crystals (3 g.; Compound D) separated {Found: Co, 19·95; NH_3, 29·03; PO_4, 32·38 (total and ionisable); H_2O, 18·64. Calc. for $[Co(NH_3)_5H_2O]PO_4,2H_2O$: Co, 20·11; NH_3, 29·05; PO_4, 32·41 (total and ionisable); H_2O, 18·45%}; when left in a desiccator over concentrated sulphuric acid, this aquopentamminocobalt phosphate dihydrate lost one molecule of water.

(3*b*) To a solution of 5 g. of a tetrammino-salt in 50 ml. of water a solution (25 ml.) of 2·64 g. of $(NH_4)_2HPO_4$ was added, and the mixed solution kept at 0° for 2 days; when carbonatotetramminocobalt(III) nitrate was used as starting material, purple crystals (2·5 g.; Compound E) separated slowly {Found: Co, 22·54; NH_3, 27·55; PO_4, 36·24 (total), 0 (ionisable); H_2O, 13·27. Calc. for $[Co(NH_3)_4PO_4],2H_2O$: Co, 22·84; NH_3, 26·38; PO_4, 36·81 (total), 0 (ionisable); H_2O, 13·96%}; both molecules of water were lost when this phosphatotetramminocobalt dihydrate was left in a desiccator over concentrated sulphuric acid. When *cis*-chloraquotetramminocobalt(III) sulphate was the starting material, a red-purple powder (4 g.) of the compound F separated rapidly as soon as the solution was cooled {Found: Co, 22·30; NH_3, 26·66; PO_4, 36·85 (total and ionisable); H_2O, 14·19. Calc. for $[Co(NH_3)_4(H_2O)_2]PO_4$: Co, 22·84; NH_3, 26·38; PO_4, 36·81 (total and ionisable); H_2O, 13·96%}.

(3*c*) The method just described, when applied to 5-g. quantities of the triammino-complexes, triaquotriamminocobalt(III) chloride or trinitrotriamminocobalt(III) yielded in each case cobalt(II) ammonium phosphate.

(4) The action of heat (at 70°, 90°, or 100°; see Table 3) on the aquopentamminocobalt(III) phosphates (Compounds A and D) or diaquotetramminocobalt(III) phosphate (Compound F) did not achieve complete removal of water before loss of ammonia commenced.

(5) Attempts to effect the oxidation of cobalt(II) phosphate in the presence of ammonium phosphate and of free ammonia, either by atmospheric oxygen or by hydrogen peroxide under conditions suggested by consideration of refs. 6. 9, 10, 11, and 13, gave cobalt(II) ammonium phosphate.

Discussion

The analytical results show that none of the pentammino-compounds prepared (A, B, or D) contained the phosphate group as a ligand. In fact all three appear to be identical ($[Co(NH_3)_5H_2O]PO_4$,1 or $2H_2O$) except that Compound D contains an extra molecule of water of crystallisation. The inference that compound D is an aquopentamminocobalt(III) phosphate dihydrate is supported by a study of its absorption spectrum, which resembles that of aquopentamminocobalt(III) chloride (Table 2). Its molar conductance (Table 1), for which we found a rather higher value than that reported by Klement,[4] appears to accord rather better, however, with the formation of 3 or 4 ions in solution than with the formation of 2 (as required by the formula), but this might arise from the reactions

$$PO_4^{3+} + H_2O \rightleftharpoons HPO_4^{2-} + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$HPO_4^{2-} + H_2O \rightleftharpoons H_2PO_4^- + OH^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The marked ease with which compounds A, B, and D lost ammonia on being heated (Table 3), together with the fact that this occurred even before all the water of crystallisation had been driven off, made it impossible to prepare the corresponding phosphato-complexes from them by the conventional method.[14]

From our results Klement's doubts [4] about Duff's report [2] of the formation of a phosphatopentamminocobalt(III) complex seem to be justified. From the failure of all the attempts to prepare them, it is evident that the phosphatopentamminocobalt(III) complexes must be extremely labile and be converted readily into the corresponding aquopentammino-phosphates $[Co(NH_3)_5H_2O]PO_4,nH_2O$ ($n = 1$ or 2).

Of the three tetrammino-compounds, E and F appear from the analyses, taken in conjunction with the conductometric (Table 1) and heating (Tables 3 and 4) experiments, to be the hydrate isomers $[Co(NH_3)_4PO_4],2H_2O$ and $[Co(NH_3)_4(H_2O)_2]PO_4$, both of which have been reported before,[4] although the direct preparation of the first of these from a

[14] Emeléus and Anderson, "Modern Aspects of Inorganic Chemistry," Routledge and Kegan Paul, London, 1952 (revised edn.), p. 108.

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tetrammino-complex had not been achieved previously. The essential differences between these compounds have now been clearly established from the studies of ionisable phosphate present, molar conductances (Table 1), absorption spectra (Table 2), and behaviour when heated (Tables 3 and 4).

The molar conductance of Compound F, like that of Compound D, is higher than expected for a compound giving two ions (Table 1), probably for the same reason (eqns. 1 and 2). However, the effect here is not so marked, possibly owing to interaction between the hydroxyl ions thus formed and the complex itself:

$$[Co(NH_3)_4(H_2O)_2]^{3+} + OH^- \rightleftharpoons [Co(NH_3)_4(OH)H_2O]^{2+} + H_2O \quad . \quad . \quad (3)$$

The small conductance found for Compound E might arise from a slight hydrolysis, which would convert it into Compound F. The very low solubility of this compound (even in the anhydrous state) in any suitable solvent makes the determination of its molecular weight by cryoscopic or similar methods impracticable. However, the following considerations suggest that as it exists in solution it should be assigned a monomeric structure with a four membered chelate ring (I).

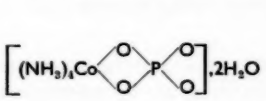
(1) The failure of both Klement [4] and ourselves to obtain pentammino-complexes containing a unidentate phosphate ligand, which would suggest that the phosphato-complexes are stable only when the phosphate group occupies two co-ordination positions; further, these must both be on the same cobalt atom, for if the formation of two co-ordinate links by the phosphate group, rather than chelation, were the important factor, then the formation of pentammino-complexes such as $[(NH_3)_5\text{–}Co\text{–}(PO_4)\text{–}Co\text{–}(NH_3)_5]^{3+}$ would be expected, but no evidence for these has been obtained.

(2) The general similarity of the absorption spectrum of Compound E to that of the carbonatotetramminocobalt(III) nitrate (Table 2) in which the carbonato-group is generally assumed to act as a chelate [15]—an assumption supported by the identification of the green anionic complex ion in the Field–Durrant solution as $[Co(CO_3)_3]^{3-}$; [16] the fact that the phosphato- and carbonato-tetrammino-complexes alone of all those studied possess strong absorption peaks at about 7000 Å (Table 2) strongly supports the assumption that they have similar structures.

(3) The direct formation of compound E from the carbonato-tetramminocobalt(III) nitrate in which the carbonato-group presumably occupies two *cis*-positions [see (2) above].

Our results for the absorption spectrum of the carbonatotetramminocobalt(III) nitrate accord with those of Yoneda and Kobayashi [17] with respect to the peaks at 3600 and 5250 Å. Our studies did not extend to the region of their peak at 2540 Å (since most of our solutions contained phosphate which absorbs strongly in this region) nor did theirs extend to the region of the peak at 7000 Å.

It is noteworthy that, whilst Compounds E and F are both prepared *by the same method* from complexes which both have a *cis*-structure, they are so different in constitution. A possible explanation lies in the fact that of the reactions

(I) 

$$[Co(NH_3)_4CO_3]^+ \xrightarrow{PO_4^{3-}} [Co(NH_3)_4PO_4] \quad . \quad (4)$$

$$[Co(NH_3)_4CO_3]^+ \xrightarrow{2H_2O} [Co(NH_3)_4(H_2O)_2]^{3+} \quad . \quad (5)$$

$$[Co(NH_3)_4(H_2O)Cl]^{2+} \xrightarrow{PO_4^{3-}} [Co(NH_3)_4PO_4] \quad . \quad (6)$$

$$[Co(NH_3)_4(H_2O)Cl]^{2+} \xrightarrow{H_2O} [Co(NH_3)_4(H_2O)_2]^{3+} \quad . \quad (7)$$

both (4) and (5) are two-stage processes, so that (5) is not more favoured than (4), whilst (7) is a single-stage substitution and is thus more favoured than the two-stage substitution of (6).

[15] Bailar (Editor), "Chemistry of the Co-ordination Compounds," Reinhold Publishing Corp., New York, 1956, pp. 32, 33, 226.
[16] McCutcheon and Schuele, *J. Amer. Chem. Soc.*, 1953, **75**, 1845.
[17] Yoneda and Kobayashi, *J. Chem. Soc. Japan*, 1954, **75**, 1192.

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Compound C, like Compound E, contains some non-ionisable phosphate and from the analyses (Table 1) appears to be $[Co(NH_3)_4HPO_4]_3PO_4$. Its molar conductance (Table 2) is also consistent with its yielding four ions; apparently any tendency for this to be increased by hydrolysis of the phosphate ion [equations (1) and (2)] is offset by ionisation of the proton on the phosphato-group:

$$[Co(NH_3)_4HPO_4]^+ + OH^- \rightleftharpoons [Co(NH_3)_4PO_4] + H_2O \quad . \quad . \quad . \quad . \quad (8)$$

The similarity of its absorption spectrum (Table 2) to that of the diaquotetramminocobalt(III) phosphate (Compound F) is surprising, but may be attributed to a rapid hydrolysis, which would convert it into Compound F, in the presence of the acid solvent used in the absorption-spectrum studies. It is evidently more stable in the neutral solutions in which the determinations of ionisable phosphate and conductivity measurements were made.

No triammino-complexes containing phosphato-groups were obtained from the reactions in solution, but the loss in weight in Compound E after prolonged heating at 110° corresponds closely to the loss of $2H_2O + NH_3$, which would indicate $[Co(NH_3)_3PO_4]$ as the product. It seems unlikely, however, that the phosphate group will occupy three co-ordination positions and the product may be more complex.

Riley [18] attributed the greater tendency of carbonate than of sulphate to occupy two co-ordination positions to the lower effective charge on the central atom in the carbonate ion, which will lead to looser binding of the electrons on the oxygen atoms and hence to their more ready utilisation in co-ordination; with the higher effective charge on the sulphur in the sulphate ion the electrons on the oxygen atoms are more tightly held. If this simple treatment, which neglects both the state of hybridisation of the central atom and the bond type (*i.e.*, possible partial double-bond character), is accepted, then the phosphate ion should show properties between those of the other two—a deduction which is in general accord with our observations. However, with respect to its ability to occupy one co-ordination position on a cobalt atom phosphate is less effective than either carbonate or sulphate.

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[*Received, May 17th,* 1957.]

[18] Riley, *J.*, 1928, 2985.

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844. *Some Fluoromolybdates*(V) *and Fluorotungstates*(V).

By G. B. HARGREAVES and R. D. PEACOCK.

Complex fluorides of quinquevalent molybdenum and tungsten involving the MoF_6^- and WF_6^- ions have been obtained from the action of the hexafluorides on the alkali iodides in liquid sulphur dioxide. Their hydrolysis is described.

ALTHOUGH oxyhalide complexes of quinquevalent molybdenum and tungsten such as $K_2Mo^VOCl_5$ and $K_2W^VOCl_5$ have been known for a long time there are no references in the literature to oxygen-free complex halides in this oxidation state. Recent work by one of us has shown that in the presence of a suitable solvent, such as liquid sulphur dioxide, rhenium hexafluoride is reduced by potassium iodide to the quinquevalent state with the formation of a complex fluoride $KReF_6$.[1] We have now discovered that this behaviour towards potassium iodide is paralleled by that of molybdenum and tungsten hexafluorides, thus enabling us to prepare fluoromolybdates(V) and fluorotungstates(V), $MMoF_6$ and MWF_6, where M is an alkali metal.

[1] Peacock, *J.*, 1957, 467.

When solutions of the reactants are brought together iodine is immediately liberated even at −60°, and the complex fluoride is precipitated. If excess of hexafluoride is present, all the alkali iodide is used and the complex salt can be obtained pure merely by

$$2MoF_6 + 2MI \longrightarrow I_2 + 2MMoF_6\downarrow$$
$$2WF_6 + 2MI \longrightarrow I_2 + 2MWF_6\downarrow$$

gradually warming it to 200° in a good vacuum to remove volatile materials. In this way the sodium, potassium, rubidium, and cæsium compounds have been isolated for each of the elements.

The fluoromolybdates(v) are all white crystals, but some specimens of the fluorotungstates(v) tend to be brown. All are stable to 250°, but above this temperature they start to attack glass. Like the corresponding rhenium compounds the salts are very sensitive to traces of moisture and rapidly become blue when exposed to the atmosphere. Water vigorously decomposes them; the fluoromolybdates(v) give a dark blue solution which slowly fades to red-brown and deposits brownish hydrated oxide MoO_2,nH_2O; the fluorotungstates(v) give an intensely blue stable solution. In neither case is there any indication of the formation of quadrivalent complex fluorides such as occurs with fluoroosmates(v),[2] fluororuthenates(v),[3] and to a less extent with fluororhenates(v). Presumably 6-co-ordinated complexes of quadrivalent molybdenum and tungsten would possess an unoccupied *d* orbital providing a ready point of attack for water molecules, a mechanism not available with rhenium or the platinum metals. Hence they would not be formed from aqueous solution, and it is interesting to note that quadrivalent chloromolybdates and chlorotungstates are also unknown.

The unit-cell sizes of both series of salts have been found from *X*-ray data and, as expected, lie close to those of the rhenium compounds (Table). Like potassium hexafluororhenate, potassium hexafluoro-molybdate and -tungstate have a slight tetragonal modification of the cubic cæsium chloride structures adopted by potassium hexafluoroniobate and -tantalate.[4] Magnetic moments at 25° have been measured for two of the salts, for $KMoF_6$ $\mu_{eff} = 1{\cdot}24$ B.M. and for $NaWF_6$ $\mu_{eff} = 0{\cdot}51$ B.M., where the spin-only value for one unpaired electron would be $\mu = 1{\cdot}78$ B.M. These low values are to be expected for Mo^{5+} and W^{5+} at ordinary temperature because of spin-orbit coupling.

Niobium and tantalum form seven- and even sometimes eight-co-ordinated complex ions, such as K_2NbF_7 and Na_3TaF_8, with fluorine, and it might be supposed that analogous molybdenum and tungsten compounds exist. We have made several attempts to isolate such complex salts, *e.g.* by fusing potassium hexafluoro-molybdate and -tungstate with potassium hydrogen difluoride and extracting the cold melt with acetone–water to remove

Unit-cell dimensions (*lengths in* Å, *with* α_0 *in parentheses*) *of some* ABF_6 *compounds*; *for others, see also refs.* 1 *and* 4.

	MoF_6^-	WF_6^-	ReF_6^-
Na	8·20	8·18	8·18
K	$a_0 = 10{\cdot}17$, $c_0 = 9{\cdot}97$	$a_0 = 10{\cdot}21$, $c_0 = 10{\cdot}09$	$a_0 = 10{\cdot}26$, $c_0 = 10{\cdot}01$
Rb	$a_0 = 5{\cdot}11$ (96·5)	$a_0 = 5{\cdot}14$ (97·3)	$a_0 = 5{\cdot}11$ (96·7)
Cs	$a_0 = 5{\cdot}29$ (96·0)	$a_0 = 5{\cdot}31$ (95·3)	$a_0 = 5{\cdot}28$ (95·9)

soluble salts. While we have been able to make a new complex oxyfluoride, K_2MoOF_5, during these experiments there has been no indication of 7- and 8-co-ordinate complexes, and it must be concluded that these are too unstable towards water to be isolated in this way. The complex oxyfluoride K_2MoOF_5 itself appears to hydrolyse readily; it is a pale green crystalline solid.

[2] Hepworth, Robinson, and Westland, *J.*, 1954, 4268.
[3] Hepworth, Peacock, and Robinson, *J.*, 1954, 1197.
[4] Cox, *J.*, 1956, 876.

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Experimental

Preparation of Quinquevalent Fluoromolybdates and Fluorotungstates.—Molybdenum and tungsten fluorides were prepared from the elements. Sulphur dioxide was dried over phosphoric acid and fractionated, and alkali iodides were dried at 100° in a vacuum before use.

The preparative method was the same as for rhenium hexafluoride, and similar rigorously dry conditions were required to obtain pure quinquevalent *fluoromolybdates* and *fluorotungstates* [Found: Mo, 38·7; F, 45·8. $KMoF_6$ requires Mo, 38·5; H, 45·8%. Found: Mo, 32·9; F, 40·2. $RbMoF_6$ requires Mo, 32·5; F, 38·6%. Found: Mo, 27·9; F, 36·4. $CsMoF_6$ requires Mo, 28·0; F, 33·3%. Found: Mo, 41·2; F, 48·9. $NaMoF_6$ requires Mo, 41·2; F, 48·4%. Found: W, 53·5; F, 33·8. KWF_6 requires W, 54·6; F, 33·8%. Found: W, 48·0; F, 28·6. $RbWF_6$ requires W, 48·0; F, 29·7%. Found: W, 42·3; F, 26·5. $CsWF_6$ requires W, 42·7; F, 27·5%. Found: W, 56·7; F, 36·5. $NaWF_6$ requires W, 57·3; F, 35·5%].

Preparation of the Complex Oxyfluoride K_2MoOF_5.—Potassium hexafluoromolybdate(v) (about 0·5 g.) was fused with a large excess of anhydrous potassium hydrogen fluoride in an atmosphere of carbon dioxide. The temperature of the melt was raised to drive off hydrogen fluoride, and, after cooling, the resulting solid was leached with acetone containing a little water until all the potassium fluoride had been dissolved out. Pale green *potassium oxypentafluoromolybdate*(v) remained (Found: Mo, 32·0; F, 32·8. K_2MoOF_5 requires Mo, 33·6; F, 33·3%).

Analysis.—The salts were always decomposed by a large excess of water, and molybdenum and tungsten oxidised to the sexavalent state with a little concentrated nitric acid. Molybdenum was estimated as the oxine derivative; tungsten was precipitated as the tannin–cinchonine complex and ignited to trioxide. In the molybdenum experiments fluorine was estimated gravimetrically as lead chlorofluoride; in the tungsten experiments fluorine was estimated volumetrically after distillation and subsequent precipitation as lead chlorofluoride. Magnetic measurements were made at the ordinary temperature, a permanent magnet being used. *X*-Ray photographs were taken on 9-cm. cameras, filtered Co-$K\alpha$ radiation being used; specimens were made up in Pyrex-glass capillaries.

We are indebted to Imperial Chemical Industries Limited, General Chemicals Division, Widnes, for the use of a fluorine cell, and to the Department of Scientific and Industrial Research for a maintenance grant to one of us (G. B. H.).

Chemistry Department, Imperial College, London, S.W.7. [*Received, June 13th,* 1957.]

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845. *Ionophoresis of Carbohydrates. Part VI.* A Steric Effect in the Reaction of Certain Pyran Derivatives with Borate Ions.*

By A. B. Foster.

The reaction of vicinal *cis*-hydroxyl groups in certain pyran derivatives, with borate ions, is hindered by a methoxyl group in vicinal *cis*-relationship. An explanation of this and related effects is suggested.

Extensive analytical use is now being made, in carbohydrate chemistry, of zone electrophoresis (ionophoresis) in alkaline borate buffers.[1] The value of the technique in providing structural information depends on an understanding of the reactions of borate ions with carbohydrates. Some progress towards this end has been made with derivatives of D-glucose,[2,3] and several applications of the technique in structural determination have been described.[4] The reaction of borate ions with certain pyran derivatives is now reported.

* Part V, *J.*, 1957, 1395.

[1] Part V of this series and references cited therein; see also Foster, *Adv. Carbohydrate Chem.*, 1957, **12**, 81.

[2] Foster, *J.*, 1953, 982.

[3] Foster and Stacey, *J.*, 1955, 1778.

[4] (*a*) Foster and Stacey, *Chem. and Ind.*, 1953, 279; cf. (*b*) Foster, *ibid.*, 1953, 591; Foster, Overend, Vaughan, and Stacey, *J.*, 1953, 3308; Bera, Foster, and Stacey, *J.*, 1955, 3788.

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The M_G value [2] has been adopted, in these investigations, as a convenient index of the intensity of reaction of a hydroxy-compound with borate ions and it connotes the mobility of the substance compared with that of D-glucose in ionophoresis on paper under standard conditions (see p. 4218). Small differences (*i.e.*, <10%) in M_G values between compounds of closely related structure are not easy to interpret since the mobility of ions of the type (A) in (1), in ionophoresis, will depend on their mass–charge ratio and on their size, which will be affected to an unknown extent by hydration. There does not appear to be selective adsorption of carbohydrates of low molecular weight on the paper during ionophoresis.[1,5] However, the significant differences in M_G values between isomeric compounds which are considered in this paper are quite large (see Table).

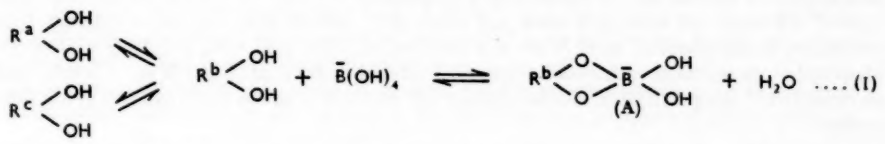
The M_G values of a series of pyran derivatives are recorded in the Table. The zero M_G values of the xylopyranose derivatives (I)—(III) indicate that vicinal *trans*-hydroxyl groups attached to a pyran ring have no affinity for borate ions. It is not possible to study this effect in pyran derivatives which contain more than three hydroxyl groups attached to separate ring carbon atoms since such compounds would be reducing sugars and capable of isomerization in solution.

M_G values of some pyran derivatives.

1 : 5-Anhydroxylitol (I)	0·00	Methyl α-D-mannopyranoside (XII)	0·42
Methyl α-D-xylopyranoside (II)	0·00	Methyl β-D-mannopyranoside (XIII)	0·31
Methyl β-D-xylopyranoside (III)	0·00	1 : 5-Anhydro-D-mannitol (XIV)	0·40
1 : 5-Anhydro-L-arabinitol (IV)	0·39	Methyl α-D-gulopyranoside (XV)	0·59
Methyl α-D-arabinopyranoside (V)	0·38	Methyl β-D-gulopyranoside (XVI)	0·72
Methyl β-D-arabinopyranoside (VI)	0·38	Methyl α-L-rhamnopyranoside (XVII)	0·31
Methyl 2-deoxy-αβ-D-ribopyranoside (VII)	0·34	Methyl β-L-rhamnopyranoside (XVIII)	0·14
Methyl α-D-lyxopyranoside (VIII)	0·45	1 : 5-Anhydro-L-rhamnitol (XIX)	0·31
Methyl β-D-lyxopyranoside (IX)	0·27	Methyl α-D-galactopyranoside (XX)	0·38
1 : 5-Anhydroribitol (X)	0·53	Methyl β-D-galactopyranoside (XXI)	0·38
Methyl β-D-ribopyranoside (XI)	0·53	1 : 5-Anhydro-D-galactitol (XXII)	0·38

The similar M_G values of methyl α- and β-D-arabinopyranoside (V) and (VI), and 1 : 5-anhydro-L-arabinitol (IV) suggest that the reactivity, towards borate ions, of the 3 : 4-hydroxyl groups in these compounds, is independent of the presence or absence of a 1-methoxyl group. Methyl α- and β-D-galactopyranoside and 1 : 5-anhydro-D-galactitol also have similar M_G values. However, in the lyxopyranosides M_G for the α-anomer (VIII) is much higher than for the β-anomer (IX), which suggests that borate ions are sterically hindered in their reaction with the 2 : 3-hydroxyl groups in the latter glycoside. In fact, in all the pyran derivatives so far examined, the presence of a methoxyl group in vicinal *cis*-relationship to vicinal *cis*-hydroxyl groups appears to hinder those hydroxyl groups in their reaction with borate ions. This structural arrangement is present in methyl β-D-lyxopyranoside (IX), methyl β-D-mannopyranoside (XIII), methyl α-D-gulopyranoside (XV), methyl β-L-rhamnopyranoside (XVIII), and (+)-bornesitol [4a] (1-*O*-methyl-*myo*-inositol).

In the pyran derivatives under consideration the probable effective reaction whereby they acquire a negative charge in the presence of borate ions is shown in equation 1

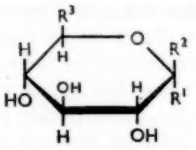


.... (1)

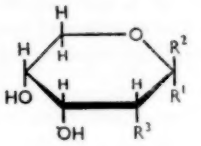
(cf. Isbell *et al.*[6]) where $R^a(OH)_2$, $R^b(OH)_2$, and $R^c(OH)_2$ are different conformations of the same molecule. The formation of "terdentate" complexes, quite different from

[5] Foster, Newton-Hearn, and Stacey, *J.*, 1956, 30.
[6] Isbell, Brewster, Holt, and Frush, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 129.

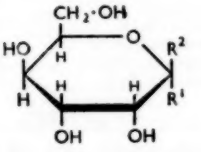
the complex A in (1), has been recognised in the reaction of borate ions with certain cyclitols.[7] The structural features necessary for terdentate complex formation suggests



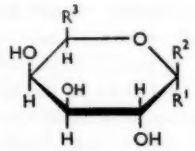
(I): $R^1 = R^2 = R^3 = H$
(II): $R^1 = OMe$, $R^2 = R^3 = H$
(III): $R^1 = R^3 = H$, $R^2 = OMe$



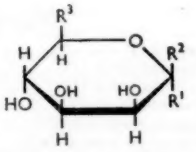
(VII): R^1, $R^2 = H$, OMe, $R^3 = H$
(X): $R^1 = R^2 = H$, $R^3 = OH$
(XI): $R^1 = H$, $R^2 = OMe$, $R^3 = OH$



(XV): $R^1 = OMe$, $R^2 = H$
(XVI): $R^1 = H$, $R^2 = OMe$



(IV): $R^1 = R^2 = R^3 = H$
(V): $R^1 = R^3 = H$, $R^2 = OMe$ (*L*-form)
(VI): $R^2 = R^3 = H$, $R^1 = OMe$ (*L*-form)
(XX): $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2{\cdot}OH$
(XXI): $R^1 = H$, $R^2 = OMe$, $R^3 = CH_2{\cdot}OH$
(XXII): $R^1 = R^2 = H$, $R^3 = CH_2{\cdot}OH$



(VIII): $R^1 = OMe$, $R^2 = R^3 = H$
(IX): $R^1 = R^3 = H$, $R^2 = OMe$
(XII): $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2{\cdot}OH$
(XIII): $R^1 = H$, $R^2 = OMe$, $R^3 = CH_2{\cdot}OH$
(XIV): $R^1 = R^2 = H$, $R^3 = CH_2{\cdot}OH$
(XVII): $R^1 = OMe$, $R^2 = H$, $R^3 = Me$ (*D*-form)
(XVIII): $R^1 = H$, $R^2 = OMe$, $R^3 = Me$ (*D*-form)
(XIX): $R^1 = R^2 = H$, $R^3 = Me$ (*D*-form)

that they are unlikely to be formed in the reaction of the pyran derivatives noted in the Table with borate ions. Clearly, the position of the equilibrium (1) will be governed, *inter alia*, by the stereochemical disposition of the hydroxyl groups in $R^b(OH)_2$ and the stability of the borate complex (A).

Note has been made [8] of the fact that the O–O distance in the preferred chair conformation of both *cyclo*hexane *cis*- and *trans*-1 : 2-diol is identical. The O–O distance in the *cis*-diol is, however, a maximum and the hydroxyl groups will approach more closely during the normal conformational oscillation. It has been suggested [9] that condensation with, for example, acetone, occurs during this process. The O–O distance in the *trans*-diol is a minimum and, as such, is too great to permit condensation with acetone. This argument also applies to the reaction of these diols with borate ions since the *cis*-diol has an M_G value of 0·11 whereas the *trans*-diol does not react with borate ions. It is of interest that Böeseken, in his classical work [10] on the reaction of boric acid with polyhydric alcohols, observed [11] no reaction with *cyclo*hexane-*cis*-1 : 2-diol in boric acid at pH 5. Clearly, and as expected,[12] the polyhydric alcohol–borate ion reaction is much more intense in alkaline media.

[7] Angyal and McHugh, *Chem. and Ind.*, 1956, 1147.
[8] Angyal and Mills, *Rev. Pure Appl. Chem.*, 1952, **2**, 185.
[9] Angyal and MacDonald, *J.*, 1952, 686.
[10] Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189.
[11] Böeseken and Giffen, *Rec. Trav. chim.*, 1920, **39**, 183.
[12] Consden and Stanier, *Nature*, 1952, **169**, 783.

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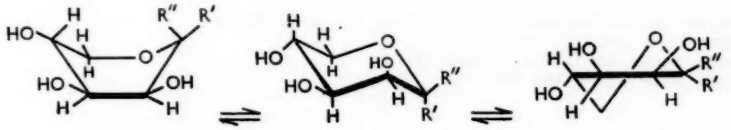
Since the geometry of the pyran ring is similar to that of the *cyclo*hexane ring,[13] the above considerations may be applied to the reaction, with borate ions, of the appropriate pyran derivatives in the Table. Thus the important point is made that, in the reaction of borate ions with pyran derivatives which contain vicinal *cis*-hydroxyl groups, conformations other than the preferred chair forms may be involved.

The O–O distance of vicinal *cis*-hydroxyl groups in the methyl D-lyxopyranosides (VIII) and (IX) will be a minimum (*i.e.*, they will be in eclipsed positions) in the boat and half-chair forms represented below (the conformation in which the pyran ring is planar is not considered). By analogy with *cyclo*hexene,[14] which can adopt either of two types of conformation structurally related to the boat and half-chair forms (XXIV) and (XXV), the half-chair conformation (XXV) is probably preferred to the boat-form (XXIV). If it is assumed that the half-chair conformation (XXV) is the one involved in complex formation with borate ions during ionophoresis, then a possible explanation may be offered for the steric effects noted above. As the preferred chair conformation (XXIII) is converted into the half-chair form (XXV), the 1-substituent R″ moves towards an eclipsed position with the 2-hydroxyl group. The dihedral angle between 2-OH and 1-R″ decreases from 60° to *ca.* 20° during this process. [The precise value of this angle depends[15] on (*a*) the magnitude, in the half-chair form (XXV), of the angles $C_{(1)}C_{(2)}C_{(3)}$ and $C_{(2)}C_{(3)}C_{(4)}$ and (*b*) the



(XXIV) (XXIII) (XXV)

Chair, boat, and half-chair forms of the methyl D-*lyxopyranosides.* α-*Anomer*, R′ = OMe, R″ = H, β-*anomer*, R′ = H, R″ = OMe. *Only one of each of the two possible boat and half-chair forms which contain eclipsed* 2 : 3-*hydroxyl groups is shown.*

degree of staggering about the ring-oxygen–$C_{(6)}$ bond.] The consequent increase in adverse non-bonded interaction will be proportional to the bulk of R″ which is OMe in methyl β-D-lyxopyranoside and H in the α-anomer; it is the β-anomer which has the low M_G value. Similar interpretations apply to the anomeric methyl D-mannopyranosides, L-rhamnopyranosides, D-gulopyranosides and 1-*O*-methyl*myo*inositol.[4a] A closely analogous conformational argument has been invoked by Lemieux and Brice[16] to relate the configuration of the 3-acetoxy-grouping with the reactivity of the 1-acetoxy-group in a series of 1 : 2-*trans* sugar acetates.

It is also possible that the above steric effect could operate in the ribopyranoside series which contains three vicinal *cis*-hydroxyl groups. Borate-complex formation of each pair of vicinal *cis*-hydroxyl groups would then be hindered by the third hydroxyl group. There is little evidence to support this although the M_G value (0·53) of 1 : 5-anhydroribitol (X) is considerably less than twice that (0·38) of 1 : 5-anhydro-L-arabinitol (IV).

The low M_G value of *cyclo*hexane-1 : 2 : 3-triol[17] and the resistance of *myo*inositol towards the formation of an *iso*propylidene derivative[9] may well be due to the operation of a steric effect similar to that described above.

The appreciably higher M_G value of methyl β-D-lyxopyranoside than of the methyl D-arabinopyranosides may be due in part to the fact that the 2-hydroxyl group, which is

[13] See Maccoll, in Klyne's "Progress in Stereochemistry," Butterworths, London, 1954, Vol. I, p. 361, for details of bond angles, bond lengths, etc.
[14] Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21.
[15] Personal communication from Dr. D. H. Whiffen.
[16] Lemieux and Brice, *Canad. J. Chem.*, 1956, **34**, 1006.
[17] Angyal and McHugh, *J.*, 1957, 1423.

involved in complex formation in the D-lyxopyranoside derivative, is more acidic than the other hydroxyl groups (cf. Wolfrom and El-Taraboulsi [18]).

Experimental

The apparatus and technique employed in ionophoresis have been described previously.[19] Ionophoreses were carried out on Whatman No. 3 paper in sodium borate [5] at pH 10 under potential gradients of 20—40 v/cm. Slight variations in M_G values were encountered in successive runs; factors which influence the M_G value have been noted in Part IV.[20] The M_G values in the Tables are comparative. The non-reducing carbohydrates and the *cyclo*hexane derivatives were detected, after ionophoresis, by means of ammoniacal silver nitrate [21] (10%).

The author acknowledges the interest of Professor M. Stacey, F.R.S., in this work and thanks Dr. D. H. Whiffen for helpful discussion. He thanks also Dr. G. R. Barker (methyl β-D-ribopyranoside), Dr. H. G. Fletcher (methyl L-rhamnopyranosides), Dr. H. S. Isbell (methyl D-lyxopyranosides, methyl D-gulopyranosides), Dr. R. W. Jeanloz (1 : 5-anhydroribitol), and Dr. W. G. Overend (methyl D-arabinopyranosides) for specimens of the derivatives mentioned. The expenses were covered by a grant from Imperial Chemical Industries Limited.

Chemistry Department, The University, Edgbaston, Birmingham, 15. [*Received, April 1st,* 1957.]

[18] Wolfrom and El-Taraboulsi, *J. Amer. Chem. Soc.*, 1953, **75**, 5350.
[19] Foster, *Chem. and Ind.*, 1952, 1050.
[20] Bourne, Foster, and Grant, *J.*, 1956, 4311.
[21] Hough, *Nature*, 1950, **165**, 400.

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846. *Esterification by Sulphuric Acid. Part II.* Ethyl Alcohol.*

By D. J. Clark and (the late) Gwyn Williams.

Velocity and equilibrium constants are reported for the solvolytic esterification of ethyl alcohol in 60—82 wt.-% aqueous sulphuric acid at 25°, and in 70—93 wt.-% aqueous sulphuric acid at 0°.

The esterification of ethyl alcohol by sulphuric acid has been investigated by Dunnicliff and his collaborators,[1] by Tian,[2] and by Deno and Newman,[3] but under conditions such that the composition of the medium changed considerably during the course of the reaction. In the present investigation the initial concentration of alcohol has been kept low (0·1M) and the progress of esterification has not significantly affected the medium. This has been achieved by analysing it for alcohol instead of for acid.

The Esterification Equilibrium.—Esterification is accompanied by a decrease in the alcohol concentration to an equilibrium value which then remains constant indefinitely in all media. The position of the equilibrium has been recorded in terms of an equilibrium ratio, K, defined by

$$K = ([EtOH]_i - [EtOH]_e)/[EtOH]_e = [EtHSO_4]_e/[EtOH]_e \quad . \quad (1)$$

where the subscripts i and e refer to initial and equilibrium concentrations, respectively.

The value of K is affected only slightly by change in the initial concentration of alcohol (Table 2), but markedly by change in the sulphuric acid–water ratio (Table 1).

* Part I, *J.*, 1956, 1304.

[1] Dunnicliff and Butler, *J.*, 1920, **117**, 649; 1921, **119**, 1384; Hamid, Singh, and Dunnicliff, *J.*, 1926, 1098.
[2] Tian, *Bull. Soc. chim. France*, 1950, 1223.
[3] Deno and Newman, *J. Amer. Chem. Soc.*, 1950, **72**, 3852.

XUM

TABLE 1. *Velocity and equilibrium constants.*

H_2SO_4 (wt.-%)	Expt. no.	$[EtOH]_i$ (M)	Esterifn. at equilm. (%)	K	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
(*a*) Temp., 0°: $[EtOH]_i = 0{\cdot}1019 \pm 0{\cdot}0005$M								
69·70	144	0·0625	38·7	0·630	0·826	1·30	0·819	1·29
	145	0·0626	38·9	0·636	0·812	1·28		
80·71	141	0·0445	56·3	1·29	22·0	17·1	22·0	17·2
	154	0·0447	56·1	1·28	22·0	17·2		
92·91	142	0·0145	85·8	6·02	459	76·4	459	76·4
(*b*) Temp., 25°: $[EtOH]_i = 0{\cdot}1018 \pm 0{\cdot}0004$M								
59·99	149	0·0773	23·8	0·312	1·91	6·11	1·91	6·15
	150	0·0777	23·5	0·308	1·90	6·18		
64·56	136	0·0715	29·8	0·425	—	—	6·41	15·1
	137	0·0714	30·0	0·428	6·41	15·1		
	151	0·0712	29·8	0·425	6·41	15·1		
69·70	132	0·0640	37·2	0·592	—	—	25·9	43·8
	133	—	—	—	26·2	44·2		
	134	0·0635	37·5	0·600	25·7	43·3		
76·79	127	0·0536	47·4	0·899	—	—	189	210
	126	—	—	—	188	210		
	128	—	—	—	190	211		
	146	0·0536	47·5	0·903	188	209		
80·71	140	0·0474	53·5	1·15	543	473	545	477
	147	0·0475	53·2	1·14	547	480		
82·20	129	0·0447	56·1	1·28	—	—	806	636
	138	0·0452	55·7	1·26	811	645		
	139	0·0449	56·0	1·27	811	638		
	152	0·0448	56·1	1·28	797	625		
92·91	143	0·0182	82·1	4·59	—	—	—	—

TABLE 2. *Effect of initial concentration of alcohol.*

In 82·20% H_2SO_4. Temp. 25°.

Expt. no.	$[EtOH]_i$ (M)	$[EtOH]_e$ (M)	Esterifn. at equilm. (%)	K	10^4k_E (min.$^{-1}$)	10^4k_H (min.$^{-1}$)	10^4k_E, mean (min.$^{-1}$)	10^4k_H, mean (min.$^{-1}$)
148	0·2038	0·0904	55·7	1·26	786	626	786	626
153	0·2041	0·0905	55·7	1·26	787	626		
138	0·1021	0·0452	55·7	1·26	811	645	806	636
139	0·1019	0·0449	56·0	1·27	811	638		
152	0·1019	0·0448	56·1	1·28	797	625		

Rates and Orders of Reaction.—The decrease in alcohol concentration was followed in each experiment to 85—90% of the equilibrium value, and over this range of reaction $\log(x_e - x)$ is accurately linear with time (Figure). This is the behaviour required for a reversible reaction of first order in both directions, the kinetic expression for which is

$$2{\cdot}303 \log\{x_e/(x_e - x)\} = (k_E + k_H)t \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where x and x_e are, respectively, the ester concentrations at time t and at equilibrium, and k_E and k_H are, respectively, the first-order velocity coefficients for esterification and hydrolysis. The possibility that the reaction is of first order in one direction but of zero order in the reverse direction, which would also yield a linear relation between $\log(x_e - x)$ and t, is excluded by the observation that $[EtOH]_e$ is proportional to $[EtOH]_i$.

For a given sulphuric acid–water medium, therefore, the rate of reaction is expressed by

$$-d[EtOH]/dt = k_E[EtOH] - k_H[EtHSO_4] \quad . \quad . \quad . \quad . \quad (3)$$

Variation of Rate with Sulphuric Acid–Water Composition.—A plot of $\log k_E(25°)$ against Hammett's acidity function H_0 is accurately linear in solutions containing less

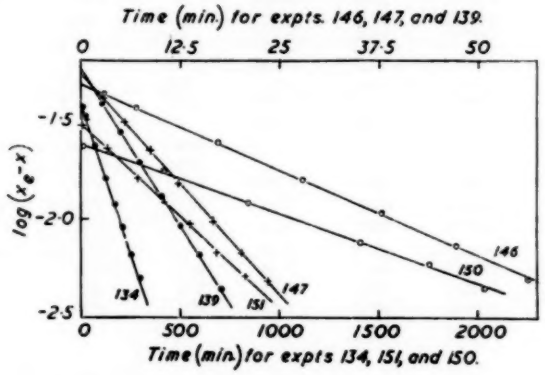
than 80% sulphuric acid but shows a small curvature at higher acidities. The equation to the best straight line through *all* the points is

$$\log k_B = -0{\cdot}926H_0 - 7{\cdot}690 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

but if points corresponding to solutions more acid than 80% sulphuric acid are omitted the best line becomes

$$\log k_B = -0{\cdot}955\ H_0 - 7{\cdot}832 \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and the coefficient of H_0 is now almost identical with that found for 2 : 4-dinitrobenzyl alcohol (−0·959; cf. Part I). The numerical terms in eqns. (4) and (5) have been calculated by the method of least squares, and the accuracy with which these expressions represent the experimental results can be judged from Table 4.



With 2 : 4-dinitrobenzyl alcohol the linear relation between log k_B and H_0 holds over the whole range of acidities in which k_B can be accurately measured and the contrary behaviour of ethyl alcohol, which must be considered a stronger base than 2 : 4-dinitrobenzyl alcohol, can plausibly be attributed to appreciable protonation in solutions containing more than 80% sulphuric acid.

Effect of Temperature.—The Arrhenius parameters, calculated from the results in Table 1, are shown in Table 3.

TABLE 3. *Parameters of equation* $k_1 = A \exp(-E/RT)$.

		Esterification		Hydrolysis	
H_2SO_4 (wt.-%)	Temp.	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)	$10^{-13}A$ (sec.$^{-1}$)	E (kcal./mole)
69·70	0·00—25·05°	0·10	22·3	0·33	22·7
80·71	,,	0·14	20·7	0·43	21·5

Reaction Mechanisms.—The reaction mechanism proposed in Part I, in which the rate of esterification is governed by the unimolecular decomposition of a protonated solvation complex of the alcohol, requires

$$\log k_B + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This equation and also eqns. (7) and (8), which refer to a bimolecular reaction between

$$\log k_B - \log a_{H_2SO_4} = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\log k_B - \log [HSO_4^-] + H_0 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

alcohol and molecular sulphuric acid present in small concentration (Part I; p. 1309), are tested in Table 4. The hypothesis of a unimolecular esterification is in best accord with

the experimental observations but the bimolecular mechanism cannot be definitely excluded.

TABLE 4.

H_2SO_4 (%)	H_0 (25°)	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
59·99	−4·32	−8·04	−8·02	−9·00	−7·72	−7·84
64·56	−4·84	−8·03	−8·26	−9·04	−7·67	−7·82
69·70	−5·50	−8·09	−8·53	−9·14	−7·68	−7·84
76·79	−6·40	−8·12	−8·77	−9·24	−7·65	−7·84
80·71	−6·93	−8·19	−8·91	−9·33	−7·68	(−7·88)
82·20	−7·17	−8·26	−8·93	−9·40	−7·73	(−7·94)

(*a*) $\log k_E(25°) + H_0$. (*b*) $\log k_E(25°) - \log a_{H_2SO_4}$. (*c*) $\log k_E(25°) - \log [HSO_4^-] + H_0$. (*d*) $\log k_E(25°) + 0{\cdot}926\ H_0$. (*e*) $\log k_E(25°) + 0{\cdot}955\ H_0$.

EXPERIMENTAL

Materials.—A commercial re-distilled absolute alcohol was used without further treatment. Analysis by dichromate oxidation indicated 99·7% of alcohol.

Kinetic Measurements.—The procedure for preparing the reaction mixtures and for carrying out the kinetic experiments was as described in Part I, p. 1311.

Analytical Method.—A 10-ml. sample of the mixture was run on to a partly frozen mixture of 0·32N-potassium dichromate (25 ml.) and sufficient water to make the final solution 4N with respect to sulphuric acid. After 18 hr. the excess of dichromate was titrated against standard ferrous ammonium sulphate, with ferroin as indicator. An acid concentration of 4N was chosen for the oxidation rather than the 6N used for the analysis of 2 : 4-dinitrobenzyl alcohol because oxidation of ethyl alcohol in 6N acid gave results which were too high (by a few tenths per cent.) in the 18-hr. oxidation period which it was convenient to adopt. In 4N-acid, oxidation of 45 mg. of ethyl alcohol is complete in 10—12 hr. at room temperature and no further dichromate is consumed during more than 72 hr. .

Analysis of numerous samples of the redistilled absolute alcohol used in these experiments has invariably returned a value of 99·7 ± 0·2% for a sample size of the order 30—50 mg., but the experimental error increases as the size of the sample is reduced, and with 7 mg. of ethyl alcohol (corresponding to 0·015M-ethyl alcohol in the mixture, the lowest concentration reached in any experiment) the error becomes ±1·0%.

Hydrolysis of ethyl hydrogen sulphate is so slow under the oxidation conditions as to introduce no appreciable error. Table 5 gives the results of an experiment in which 0·1036M-ethyl alcohol in 87·08% sulphuric acid was allowed to attain equilibrium (165 min.) at 25°, samples then being analysed in the usual way but with an acid concentration of 6N and with varying oxidation periods. In 4N-acid hydrolysis will be still slower.

TABLE 5.

Oxidation time (hr.)	2·9	3·1	21·6	22·0	69	69	192	192
10^2[EtOH] (M)	3·47	3·47	3·48	3·48	3·47	3·47	3·54	3·56
10^2[$EtHSO_4$] (M)	6·89	6·89	6·88	6·88	6·89	6·89	6·82	6·80

Equilibrium Constants.—The equilibrium concentration of alcohol was in some cases determined by a separate experiment but more usually the last two samples from the reaction mixture were used for this purpose.

Tian [2] has shown that, for aliphatic alcohols higher than ethyl, esterification is accompanied or followed by a side-reaction so that no stable equilibrium is reached, and the same is true for 2 : 4-dinitrobenzyl alcohol in media containing more than 80% of sulphuric acid. With ethyl alcohol, however, the equilibrium concentration, once established, is maintained indefinitely in all media. For example, in expt. 143 (92·91% H_2SO_4 at 25°) eight samples taken at intervals between 0·2 and 627 hr. gave $[EtOH]_e$ = 0·0182, 0·0182, 0·0182, 0·0182, 0·0182, 0·0182, 0·0183, and 0·0183.

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847. *Infrared Spectra of Some Nitrato-co-ordination Complexes.*

By B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm.

The infrared absorption spectra of a number of nitrato-complexes of metals have been examined in the region between 4000 and 700 cm.$^{-1}$. Assignments have been made for vibrations characteristic of the co-ordinated nitrato-group. Strong absorption bands, which do not occur in ionic nitrates, appear in the regions 1530—1480 and 1290—1250 cm.$^{-1}$. The absorption arising from the vibration ν_1, theoretically inactive for NO_3^- ion, occurs as a strong peak in the nitrato-complexes within the range 1034—970 cm.$^{-1}$, here designated ν_2 and due to $^-O^-NO_2$ stretching.

Recently Shimura and Tsuchida [1] examined some nitratoammino-complexes of tervalent cobalt in the visible and ultraviolet region. However, no data on infrared absorption of nitrato-complexes have been reported. The present work was undertaken to ascertain whether there were features in the infrared spectra which could be used to distinguish co-ordinated nitrato-groups from the nitrate ion in metal complexes.

Experimental

Determination of Spectra.—A Grubb-Parsons double-beam infrared spectrometer, equipped with an S3A monochromator and a rock-salt prism, was used. The samples were ground in an agate vibration mill. The mulling agents used were Nujol (2—15 μ) and hexachlorobutadiene (5—8 μ). The latter was used for the region obscured by Nujol absorption bands.

The samples were examined between rock-salt plates; in cases where it appeared likely that there might be some replacement of a nitrato-group by chloride from the rock-salt plates, the plates used were coated with a fine film of polystyrene, as supplied by Grubb-Parsons.

Preparation of Compounds.—Hexamminocobalt(III) chloride was prepared as described by Gmelin [2] (Found: Cl, 39·7; Co, 22·2. Calc. for $H_{18}N_6Cl_3Co$: Cl, 39·8; Co, 22·0%). From it was prepared hexamminocobalt(III) nitrate by treatment with silver nitrate [3] and subsequent recrystallization (Found: Co, 17·0. Calc. for $H_{18}O_9N_9Co$: Co, 17·0%). Carbonatotetramminocobalt(III) nitrate hemihydrate was prepared as described by Gmelin [4] (Found: Co, 22·7. Calc. for $CH_{12}O_6N_5Co,\frac{1}{2}H_2O$: Co, 22·8%), and *dinitratotetramminocobalt*(III) *nitrate monohydrate* was prepared from it by treatment with nitric acid [5] (Found: Co, 17·6; H_2O, 5·4. Calc. for $H_{14}O_{10}N_7Co$: Co, 17·8; H_2O, 5·4%). Nitratopentamminocobalt(III) nitrate was prepared as described by Gmelin [6] (Found: Co, 17·8. Calc. for $H_{15}O_9N_8Co$: Co, 17·9%). This (0·7 g.) was dissolved in cold water (175 ml.) containing a few drops of nitric acid, and treated with a solution of potassium chloroplatinate(II) (0·9 g.) in water (30 ml.). *Nitratopentamminocobalt*(III) *chloroplatinate*(II) was precipitated as fine pinkish-brown crystals, which were filtered off, and washed with water, then acetone (Found: Cl, 25·7; N, 15·8. $H_{15}O_3N_6Cl_4CoPt$ requires Cl, 26·1; N, 15·5%).

Nitratochlorotetramminocobalt(III) *chloride hemihydrate.* Dinitratopentamminocobalt(III) nitrate monohydrate (2 g.) was treated on a filter-paper with 1N-sulphuric acid (30 ml.), warmed to 30°. The filtrate was allowed to run into ice-cold concentrated hydrochloric acid (100 ml.). The *compound* was obtained as a purplish-pink precipitate, which was washed with ice-cold hydrochloric acid, then acetone (Found: Co, 21·3; Cl, 26·5; N, 25·2; H_2O, 3·9. $H_{12}O_3N_5Cl_2Co,\frac{1}{2}H_2O$ requires Co, 21·9; Cl, 26·4; N, 26·0; H_2O, 3·3%).

Dinitratodiaquopalladium(II). Palladium was dissolved in concentrated nitric acid, and the solution evaporated to small bulk. The mixture was cooled, and the light brown crystals filtered off, pressed almost dry, and dried *in vacuo* over sodium hydroxide (Found: Pd, 40·0. Calc. for $H_4O_4N_2Pd$: Pd, 40·0%).

[1] Shimura and Tsuchida, *J. Chem. Soc. Japan*, 1956, **77**, 734.
[2] Gmelin, "Handbuch der anorganische Chemie," Verlag Chemie, Berlin, 1930, **58**, *B*, 51.
[3] *Idem, ibid.*, p. 49.
[4] *Idem, ibid.*, p. 279.
[5] *Idem, ibid.*, p. 227.
[6] *Idem, ibid.*, p. 145.

XUM

Dinitrato-2 : 2′-dipyridylpalladium(II) was prepared as described by Livingstone [7] (Found: N, 14·0; Pd, 27·2. Calc. for $C_{10}H_8O_6N_4Pd$: N, 14·6; Pd, 27·5%).

cis-*Tetranitratodiamminoplatinum*(IV). *cis*-Dichlorodiamminoplatinum(II), dissolved in dilute nitric acid, was treated with 2 equiv. of silver nitrate. The silver chloride was filtered off, and the platinum oxidized to platinum(IV) by adding concentrated nitric acid and evaporating the solution almost to dryness, pale yellow crystals being deposited (Found: Pt, 40·4. Calc. for $H_8O_{12}N_6Pt$: Pt, 40·8%).

trans-Tetranitratodiamminoplatinum(IV) was prepared analogously (Found: Pt, 41·1%).

Potassium hexanitratocerate(IV). Precipitated ceric oxide was dissolved in hot 8N-nitric acid containing 2 equiv. of potassium nitrate. The solution was concentrated to small bulk and cooled. The *product* was filtered off and recrystallized from 8N-nitric acid. The orange crystals were pressed almost dry and dried *in vacuo* over sodium hydroxide (Found: Ce, 23·1. $O_{18}N_6CeK$ requires Ce, 23·7%).

Dinitratobis(triethylphosphine)nickel(II). A sample of this compound was kindly given by Dr. N. S. Gill (Found: C, 35·5; H, 7·4. Calc. for $C_{12}H_{30}O_6N_2P_2Ni$: C, 34·4; H, 7·2%).

Results and Discussion

The frequencies of the absorption peaks of the compounds examined are listed in Table 1. The spectrum of hexamminocobalt(III) chloride was obtained for comparison to ascertain which absorption bands arise from the nitrate group in the cobaltammine complexes studied. In the infrared spectrum of $[Co(NH_3)_6]Cl_3$ there are no sharp bands in the vicinity of 825 and 1050 cm.$^{-1}$, where intense absorption occurs in the cobaltammine nitrates. However, there is a strong sharp peak at 1328 cm.$^{-1}$, with two weak shoulders on the higher-frequency side, arising from the symmetric deformation vibration of the NH_3 group. This band is obscured by a strong band when the compounds contain the NO_3^- ion.

The absorption frequencies [9] for the NO_3^- ion, which belongs to the point group D_{3h} (the latter includes all plane trigonally symmetric XY_3 type molecules),[9] are listed in Table 1 together with the vibration types, activity in the Raman and infrared spectra, and assignments.

Table 1.

Type [14]	Raman	Infrared	NO_3^-	cm.$^{-1}$	Assignment
A_1'	a	ia	ν_1	1050	N–O stretching
A_2''	ia	a	ν_2	831	NO_3 deformation
E'	a	a	ν_3	1390	NO_3 asym. str.
E'	a	a	ν_4	720	Planar rocking

a = active; ia = inactive.

Miller and Wilkins [10] reported the spectra of ten ionic nitrates [*e.g.*, KNO_3 and $Co(NO_3)_2,6H_2O$], in all of which ν_3 appears very strongly in the range 1390—1350 cm.$^{-1}$, and ν_2 (of medium intensity) in the range 836—815 cm.$^{-1}$. It has been observed by Mizushima and Quagliano [11] that, in addition to the active frequencies for the NO_3^- ion, the forbidden frequency (ν_1) appears in the infrared spectrum of compounds when the nitrate ion is outside the co-ordination sphere. They attribute this to deformation of the ion in the field of the crystal. Calcium nitrate, alone of the nitrates investigated by Miller and Wilkins,[10] shows a weak absorption at 1044 cm.$^{-1}$, which corresponds to the forbidden frequency ν_1 for the nitrate ion. This forbidden frequency in the region of 1050 cm.$^{-1}$ appears weakly in all the complexes containing the free nitrate ion listed in Table 3.

In complexes where the nitrato-group is covalently bound through one oxygen atom, the symmetry is lowered and the group now belongs to the point group C_{2v} and has the vibration types and properties listed in Table 3.

The NO_2 bending and planar rocking vibrations of the ONO_2 group would give

[7] Livingstone, *J. Proc. Roy. Soc. New South Wales*, 1952, **86**, 35.

rise to frequencies beyond the region observed during this investigation. The above assignments have been made by reference to the spectrum of methyl nitrate.[8]

The strong absorption which occurs in $[Pd(H_2O)_2(NO_3)_2]$ and in $[Ni(PEt_3)_2(NO_3)_2]$ at about 1360 cm.$^{-1}$ can be ascribed to instability of these two complexes leading to some decomposition.

TABLE 2. *Infrared absorption bands.*

	ν_4	NH_3 and $\nu_3NO_3^-$	ν_1	$\nu_1NO_3^-$	ν_2	NH_3 and $\nu_2NO_3^-$	ν_6
$[Co(NH_3)_6](NO_3)_3$		1376s 1299sh		1045w		823s	
$[Co(NH_3)_4CO_3]NO_3,\frac{1}{2}H_2O$		1416sh 1391s 1344sh		1047w		831m 818m	
$[Co(NH_3)_4(NO_3)_2]NO_3,H_2O$	1499s	1393s 1348sh	1266s	1049w	1010s	825m	800w
$[Co(NH_3)_5NO_3](NO_3)_2$	1495s	1377vs 1330sh	1269s	1052w 1032w	1011s	828s	803w
$[Co(NH_3)_4NO_2{\cdot}Cl]Cl,\frac{1}{2}H_2O$	1488s	1387m 1314s	1282s		1013s	825w	797w
$[Co(NH_3)_5NO_2]PtCl_4$	1481m	1362w 1339m 1326m	1269s	1027w	1012s		796s
$[Pd(NO_3)_2$ dipy]	1517s 1502s	1319w	1292sh 1274s 1250sh		989s 979s 975s		801s
$[Pd(NO_3)_2(H_2O)_2]$	1502s	1362vs 1307s	1274s		988vs		797sh 784s
$[Ni(PEt_3)_2(NO_3)_2]$	1513m	1418sh 1359vs	1272s		1018s		805m
cis-$[Pt(NH_3)_2(NO_3)_4]$	1529s	1387m 1339w 1326w	1290sh 1276sh 1264s		980s 956s	823s	781w
trans-$[Pt(NH_3)_2(NO_3)_4]$	1522s	1330m	1253s		970bs	821m 816m	
$K_2[Ce(NO_3)_6]$	1531s	1387w	1290s 1277sh		1034vs		804s 799sh
CH_3NO_3	1672vs		1287s		854s		759m

w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, bs = broad, strong, dipy = 2 : 2′-dipyridyl.

Bands at 901 and 904 cm.$^{-1}$ were observed in $[Pd(NO_3)_2(H_2O)_2]$ and *trans*-$[Pt(NH_3)_2(NO_3)_4]$, respectively. These are not assigned at present.

TABLE 3.

Type [14]	Raman	Infrared	ONO_2	cm.$^{-1}$	Assignment
A_1	a	a	ν_3	not obs.	NO_2 bending
A_1	a	a	ν_1	1290—1253	NO_2 sym. str.
A_1	a	a	ν_2	1034—970	N–O str.
B_2	a	a	ν_6	800—781	Nonplanar rock.
B_1	a	a	ν_4	1531—1481	Asym. str.
B_1	a	a	ν_5	not obs.	Planar rock.

The frequency of the N–O stretching vibration would be expected to vary considerably in going from an electrostatically to a covalently bound nitrato-group. The frequency of the absorption band (ν_2) of the nitrato-complexes was found to lie between the extremes, on the one hand, of the observed frequency (1050 cm.$^{-1}$) for an ionic nitrate, and, on the other hand, of the observed frequency (854 cm.$^{-1}$) of covalent $\cdot O\cdot NO_2$ in methyl nitrate. In methyl nitrate it is difficult to imagine the $\cdot O\cdot NO_2$ group as being anything other than covalently bound, whereas in metal complexes the bonding between the nitrato-group and

[8] Brand and Cawthon, *J. Amer. Chem. Soc.*, 1955, **77**, 319.
[9] Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand, New York 1945, p. 178.
[10] Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253.
[11] Mizushima and Quagliano, *J. Amer. Chem. Soc.*, 1953, **75**, 4870.

the metal could be regarded as being at least partly electrostatic. This means that the amount of overlap between the orbital of the oxygen of the $\cdot O \cdot NO_2$ group and that of the metal atom is smaller than in the case of a strong covalent bond. Using the frequency of the absorption band (ν_2) as a criterion of the degree of covalent character of the metal–nitrate bond, we obtain the following series: $Ce^{IV} < Ni^{II} < Co^{III} < Pd^{II} < Pt^{IV}$. The results obtained for the compounds $[Pd(H_2O)_2(NO_3)_2]$ and $K_2[Ce(NO_3)_6]$ indicate that in them the nitrato-groups are not purely ionic. Since this work was done the spectrum of $Zn_3Pr_2(NO_3)_6,24H_2O$ has been reported.[12] It displays similar splitting of ν_3 into (*a*) and (*b*) with frequencies 1481—1475 and 1357—1323 cm.$^{-1}$, respectively. The absorption band ν_2 appears at 1047 cm.$^{-1}$. This frequency indicates that the degree of covalent character of the metal–nitrate bond for Pr^{III} is less than that for Ce^{IV}.

The splitting of the bands (ν_4), (ν_1), and (ν_2), observed in [Pd dipy $(NO_3)_2$], arises from the lower symmetry of this compound owing to the two nitrato-groups' being in *cis*-positions; similar phenomena have been observed [13] for *cis*-dinitro-metal complexes.

Finally, strong absorption bands in the regions 1530—1480 and 1290—1250 cm.$^{-1}$ in metal compounds containing an NO_3 group, are indicative that the nitrato-group is co-ordinated to the metal atom.

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[12] Häfele, *Z. Physik*, 1957, **148**, 262.
[13] Gatehouse, unpublished work.
[14] Meister *et al.*, Research Publications, Illinois Institute of Technology, Vol. 6, No. 1, Jan. 1948.

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848. *The Reaction of Imidates with α-Amino-acetals and α-Amino-aldehydes.*

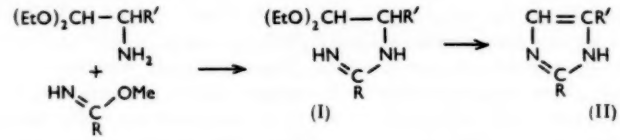
By ALEXANDER LAWSON.

α-Amino-aldehydes and α-amino-acetals react with imidates to give the corresponding 2 : 5-disubstituted glyoxalines (II). The reaction mechanism is discussed.

2-ALKYL- and 2-aryl-substituted glyoxalines can be prepared by the oldest method [1,2] used for the synthesis of the glyoxaline ring, *i.e.*, reaction of the appropriate aldehyde with a dicarbonyl compound and ammonia, and this reaction has been applied with many modifications, one of which, involving the use of an α-hydroxy-ketone and cupric acetate [3] instead of the dicarbonyl compound, has been widely used. Other methods utilise the reaction between α-amino-nitriles and aldehydes [4] and between α-halogeno-ketones and benzamidine.[5] Cornforth and Huang [6] in their investigations of oxazole syntheses showed that condensing the hydrochloride of aminoacetone or ethyl α-aminoacetoacetate with imidates produced a mixture of an oxazole and a glyoxaline, the former being convertible by ammonia under pressure into a glyoxaline relatively easily when the 4-carboxylic acid

[1] Radziszewski, *Ber.*, 1882, **15**, 1493.
[2] Japp and Robinson, *ibid.*, p. 1268.
[3] Weidenhagen and Herrmann, *Ber.*, 1935, **68**, 1953.
[4] Minovici, *Ber.*, 1896, **29**, 2097.
[5] Kunckell, *Ber.*, 1901, **34**, 637.
[6] Cornforth and Huang, *J.*, 1948, 1960.

group was present. The same authors reported that attempts to condense methyl benzimidate with aminoacetaldehyde hydrochloride gave a tar from which only triphenyltriazine, derived merely from the aminoacetaldehyde, could be isolated.



An examination of this reaction between a number of α-amino-aldehydes and methyl or ethyl benzimidate has now shown that in all cases condensation takes place readily in aqueous ethanol at neutral pH to give the corresponding 2-phenylglyoxaline (II; R = Ph). Using the products obtainable by the Akabori reduction procedure from α-amino-esters gives yields which, except for glycine and serine, are quite satisfactory; and with certain amino-acids (alanine, α-phenylglycine, α-*p*-hydroxyphenylglycine, phenylalanine, and tyrosine) the bulk of the product crystallises as the 2 : 4(5)-disubstituted glyoxaline hydrochloride on addition of hydrochloric acid to the reaction mixture after 3½ hours' heating. No evidence of the alternative mode of ring closure to oxazoles was obtained.

The synthesis of 4(5)-methyl-2-phenylglyoxaline, for example, accomplished by Cornforth and Huang[6,7] in three stages from hippuric acid by way of 4 : 5-dihydro-5-(1-hydroxyethylidene)-2-phenyloxazol-4-one, is much more readily attained in two stages by the action of methyl benzimidate on the solution of α-aminopropionaldehyde resulting from the reduction of alanine ethyl ester.

The use of aminoacetaldehyde diethyl acetal in the condensation with methyl benzimidate gives an 85% yield of 2-phenylglyoxaline and the reaction also takes place with methylaminoacetaldehyde acetal, though not quite so readily.

With imidates such as methyl hexanimidate, the reaction with α-amino-aldehydes does not proceed quite so satisfactorily, owing no doubt to the instability of the imidate,

TABLE 1. 2 : 4(5)-*Disubstituted glyoxalines* (II).

Parent amino-acid	R	R′	Form	M. p.	Yield [a] (%)	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
Glycine	Ph	H	Leaflets [a]	148°	18	—	—	—	—	—
Alanine	Ph	Me	Needles [a]	184	46	—	—	—	—	—
Alanine	C_5H_{11}	Me	Oil	—	47	$C_9H_{16}N_2$	71·0	10·5	71·1	10·6
Aminomalonic	Ph	CO_2Et	Needles [b]	174	—	$C_{12}H_{12}O_2N_2$	66·8	5·7	66·7	5·5
α-Aminobutyric	Ph	Et	Needles [a]	170	53	$C_{11}H_{12}N_2$	76·9	6·8	76·8	7·0
Aspartic	Ph	$CH_2{\cdot}CO_2Et$	Prisms [a]	98	37	$C_{13}H_{14}O_2N_2$	67·6	6·0	67·8	6·1
Glutamic	Ph	$[CH_2]_2{\cdot}CO_2Et$	Prisms [a]	123	46	$C_{14}H_{16}O_2N_2$	68·7	6·5	68·9	6·6
Serine	Ph	$CH_2{\cdot}OH$	Leaflets [b]	170	10	$C_{10}H_{10}ON_2$	68·9	5·6	69·0	5·7
α-Phenylglycine	Ph	Ph	Needles [a]	189	31	—	—	—	—	—
Phenylalanine	Ph	CH_2Ph	Rosettes [b]	166	33	$C_{16}H_{14}N_2$	81·9	6·0	82·0	6·0
Tyrosine	Ph	$CH_2{\cdot}C_6H_4{\cdot}OH$	Prisms [a]	245	34	$C_{16}H_{14}ON_2$	76·6	5·6	76·8	5·6
α-*p*-Hydroxyphenylglycine	Ph	$C_6H_4{\cdot}OH$	Needles [b]	221	42	$C_{15}H_{12}ON_2$	76·3	5·2	76·2	5·1

[a] From benzene. [b] From EtOH. [c] Based on amino-acid used.

but it was possible to isolate small yields of the 2-pentylglyoxalines (II; R = C_5H_{11}) corresponding to all the amino-aldehydes which were investigated.

Schipper and Day[8] offer an explanation of the ring closure of α-amino-ketones with methyl benzimidate to glyoxalines based on mechanisms reported for analogous reactions.[9] They postulate as the first step the addition of the polarised =NH group of the imidate

[7] Cornforth and Cookson, *J.*, 1952, 1085.
[8] Schipper and Day, in Elderfield's "Heterocyclic Compounds," Wiley, New York, 1957, Vol. V, p. 220.
[9] McCoy and Day, *J. Amer. Chem. Soc.*, 1943, **65**, 2159.

to the carbonyl group, followed by the addition of the amino-group across the =C=N– bond so formed. Such a mechanism does not seem applicable to the reaction between the imidate and α-amino-acetal. This reaction proceeds in two stages, the first at neutrality, in which the *N*-substituted amidine (I; R = Ph, R′ = H), isolable as its picrolonate, is formed, and the second, under the influence of 5N-acid, in which presumably hydrolysis of the acetal group takes place and the amidine undergoes ring closure to give the glyoxaline (II; R = Ph, R′ = H) A similar reaction course can presumably also take place when the amino-acetal is replaced by an amino-aldehyde. Schipper and Day's mechanism is likewise not applicable in the formation of 2-aminoglyoxalines from α-amino-acetals and cyanamide,[10] where the acetal guanidine salt formed as an intermediate is actually isolated.

TABLE 2. *Hydrochlorides of* 2 : 4(5)-*disubstituted glyoxalines* (II).

					Found (%)		Required (%)	
R	R′	Form	M. p.	Formula	C	H	C	H
Ph	Me	Needles †	137° *	$C_{10}H_{10}N_2,HCl,H_2O$	56·2	6·1	56·4	6·1
Ph	$CH_2{\cdot}CO_2Et$	Needles †	146	$C_{13}H_{14}O_2N_2,HCl$	58·3	5·6	58·5	5·6
Ph	$CH_2{\cdot}CO_2H$	Needles *	202	$C_{11}H_{10}O_2N_2,HCl,H_2O$	51·4	4·9	51·4	5·1
Ph	$[CH_2]_2{\cdot}CO_2Et$	Needles †	170	$C_{14}H_{16}O_2N_2,HCl$	59·8	6·2	59·8	6·1
Ph	$[CH_2]_2{\cdot}CO_2H$	Needles *	144 *	$C_{12}H_{12}O_2N_2,HCl,H_2O$	53·0	5·5	53·2	5·5
C_5H_{11}	Ph	Prisms †	129	$C_{14}H_{18}N_2,HCl$	66·9	7·8	67·0	7·6
Ph	Ph	Needles †	273 *	—	—	—	—	—
Ph	CH_2Ph	Needles ‡	112	$C_{16}H_{14}N_2,HCl,H_2O$	66·1	5·7	66·4	5·9
Ph	$C_6H_4{\cdot}OH$	Needles †	263	$C_{15}H_{12}ON_2,HCl$	65·8	4·9	66·1	4·8
Ph	$CH_2{\cdot}C_6H_4{\cdot}OH$	Needles †	252 *	$C_{16}H_{14}ON_2,HCl,H_2O$	62·6	5·6	63·0	5·6

* From H_2O. † From EtOH. ‡ From aq. acetone–ether. * With decomp.

EXPERIMENTAL

Preparation of 2 : 4(5)-*Disubstituted Glyoxalines from Amino-acids.*—The amino-acid (10 g.) was esterified with ethanol and reduced with sodium amalgam at pH 4 according to the Akabori procedure.[11] The resulting solution, after filtration, was evaporated to dryness under reduced pressure and the residue extracted with ethanol. The filtered ethanolic solution was again evaporated under reduced pressure and the residue taken up in ethanol and filtered. An aliquot part of this solution of the amino-aldehyde was mixed with methyl benzimidate or hexanimidate (1 mol.), and the pH adjusted if necessary to 7 by the addition of acetic acid. The mixture, after 1 hr. at room temperature, was heated on the steam-bath for 3—4 hr. by which time most of the ethanol had evaporated. Trituration with dilute hydrochloric acid and cooling to 0° gave, in a number of cases, crystals of the glyoxaline hydrochloride which were removed and recrystallised from the solvent mentioned in Table 2. From the aqueous solutions of the hydrochlorides the free bases were liberated by sodium hydroxide, and, if solid, purified by crystallisation. When no precipitate of the hydrochloride was obtained on addition of hydrochloric acid, the solution was made alkaline with sodium hydroxide and extracted with ether. Removal of the ether gave the free bases described in Table 1. In the cases of ethyl 2-phenyl-4-glyoxalinyl-acetate and -propionate (from aspartic and glutamic acid, respectively) it was more convenient to distil the bases at 1 mm. before crystallising them. Of the derivatives mentioned in Table 3, the picrolonates crystallised most readily.

Preparation of Glyoxalines from α-Amino-acetals.—The acetal (0·01 mole) was heated with the imidate (0·01 mole) and glacial acetic acid (0·02 mole) on the steam-bath for 3 hr. At this stage extraction of the basic product from the dark mixture, to which water and sodium hydroxide had been added, gave, in the case of α-aminoacetaldehyde diethyl acetal, an oil which formed *α-benzamidinoacetaldehyde diethyl acetal picrolonate*, prisms (from ethanol), m. p. 139° (Found: C, 55·1; H, 5·6. $C_{23}H_{28}O_7N_6$ requires C, 55·2; H, 5·6%). The reaction mixture (above) was heated with 5N-hydrochloric acid (4 ml.) for a further 0·5 hr., water was added, and the solution evaporated under reduced pressure. The residue was dissolved in water and extracted with ether to remove some benzamide in the case of benzimidate. After basification with sodium hydroxide the glyoxaline was extracted with ether and, in the case of 2-phenylglyoxaline, the residue, after evaporation of the ether, was recrystallised from benzene. The

[10] Lawson, *J.*, 1956, 307.
[11] Lawson, *J.*, 1957, 1443.

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TABLE 3. *Derivatives of 2 : 4(5)-disubstituted glyoxalines.*

Compound	Form	M. p.	Formula	Found (%) C	Found (%) H	Reqd. (%) C	Reqd. (%) H
4(5)-Methyl-2-phenylglyoxaline picrate	Prisms †	201°	$C_{16}H_{13}O_7N_5$	49·3	3·2	49·6	3·4
4(5)-Methyl-2-pentylglyoxaline picrolonate	—†	190	$C_{19}H_{24}O_5N_6$	54·8	5·9	54·8	5·8
4(5)-Ethyl-2-phenylglyoxaline picrate	Prisms †	203	$C_{17}H_{15}O_7N_5$	50·5	4·0	50·8	3·7
4(5)-Ethyl-2-phenylglyoxaline oxalate	Needles *	197	$C_{13}H_{14}O_4N_2$	59·1	5·4	59·5	5·4
4(5)-Ethoxycarbonyl-2-phenylglyoxaline picrate	Needles *	187	$C_{18}H_{15}O_9N_5$	48·5	3·5	48·5	3·3
4(5)-Hydroxymethyl-2-phenylglyoxaline picrolonate	—†	230	$C_{20}H_{16}O_6N_6$	54·8	4·4	54·8	4·1
Ethyl 2-phenyl-4-glyoxalinylpropionate picrate	Needles †	188	$C_{20}H_{19}O_9N_5$	50·5	4·3	50·7	4·0
Ethyl 2-phenyl-4-glyoxalinylpropionate picrolonate	Needles †	186	$C_{24}H_{24}O_7N_6$	56·9	4·9	56·8	4·7
Ethyl 2-phenyl-4-glyoxalinylacetate picrate	Needles †	164	$C_{19}H_{17}O_9N_5$	49·8	3·7	49·7	3·7
Ethyl 2-phenyl-4-glyoxalinylacetate picrolonate	Needles †	212 *	$C_{23}H_{22}O_7N_6$	55·6	4·3	55·8	4·5
2-Pentyl-4(5)-phenylglyoxaline oxalate	Needles †	148	$C_{16}H_{20}O_4N_2{\cdot}H_2O$	61·2	6·9	59·7	6·8
2-Pentyl-4(5)-phenylglyoxaline picrolonate	Needles †	167	$C_{24}H_{26}O_8N_6$	60·0	5·6	60·3	5·5
2 : 4(5)-Diphenylglyoxaline nitrate	Needles †	115	$C_{15}H_{12}N_2,HNO_3,H_2O$	59·7	4·8	59·8	5·0
" " picrate	Needles †	193	$C_{21}H_{15}O_7N_5$	55·8	3·3	56·1	3·3
4(5)-Benzyl-2-phenylglyoxaline picrate	Needles †	172	$C_{22}H_{17}O_7N_5$	57·0	3·7	57·0	3·7
4(5)-Benzyl-2-pentylglyoxaline oxalate	Prisms *	140	$C_{17}H_{22}O_4N_2$	64·5	6·7	64·2	6·9
4(5)-Benzyl-2-pentylglyoxaline picrolonate	Needles †	133	$C_{25}H_{28}O_8N_6$	60·9	5·8	61·0	5·7
4(5)-*p*-Hydroxyphenyl-2-phenylglyoxaline picrate	Needles †	222	$C_{21}H_{15}O_8N_5$	54·6	3·5	54·2	3·2
4(5)-*p*-Hydroxybenzyl-2-phenylglyoxaline picrolonate	Needles †	247 *	$C_{24}H_{22}O_6N_6$	60·4	4·2	60·7	4·3

* From H_2O. † From EtOH. * With decomp.

hydrochlorides were obtained from the bases by treatment of the ether solution with anhydrous hydrogen chloride. In this way were obtained: 2-pentylglyoxaline (75%) [picrolonate, m. p. 190° (from acetone) (Found: C, 53·4; H, 5·3. Calc. for $C_{19}H_{22}O_5N_6$: C, 53·7; H, 5·5%)]; 2-phenylglyoxaline (85%), leaflets (from benzene), m. p. 148° (Found: C, 74·8; H, 5·6. Calc. for $C_9H_8N_2$: C, 75·0; H, 5·6%) [*hydrochloride*, prisms (from ethanol), m. p. 154° (Found: C, 54·2; H, 5·3. $C_9H_8N_2,HCl,H_2O$ requires C, 54·4; H, 5·5%)]; 1-methyl-2-pentylglyoxaline (33%), an oil [*picrolonate*, needles, (from ethanol), m. p. 146° (Found: C, 54·6; H, 5·6. $C_{19}H_{24}O_5N_6$ requires C, 54·8; H, 5·8%)]; 1-methyl-2-phenylglyoxaline (42%), an oil [*hydrochloride*, prisms (from ethanol), m. p. 178° (Found: C, 56·6; H, 6·1. $C_{10}H_{10}N_2,HCl,H_2O$ requires C, 56·5; H, 6·1%); picrate, needles (from ethanol), m. p. 135° (Found: C, 49·4; H, 3·3. Calc. for $C_{16}H_{13}O_7N_5$: C, 49·6; H, 3·4%)]. 1-Methyl-2-pentylglyoxaline, an oil (30%) [*picrolonate*, needles, (from ethanol), m. p. 146° (Found: C, 54·5; H, 5·6. $C_{19}H_{24}O_5N_6$ requires C, 54·8; H, 5·8%)].

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849. *Charge-transfer Spectra involving Saturated Hydrocarbons.*

By D. F. Evans.

The strong ultraviolet absorption of iodine dissolved in a number of saturated hydrocarbons has been measured, and is discussed in connection with recent theories of charge-transfer spectra. A distinct band around 2400 Å is observed (at room temperature or −127°) with hydrocarbons containing a *cyclo*hexane ring, thus indicating that a *cyclo*hexane ring has appreciably greater donor properties than an open-chain saturated hydrocarbon or a *cyclo*pentane ring. The ultraviolet spectrum of tetranitromethane in 2 : 2 : 4-trimethylpentane or *cyclo*hexane shows considerable long-wavelength absorption not found in the vapour phase. This is attributed to charge-transfer transitions, and, in agreement with this, no comparable effect is observed with nitromethane.

Evidence has been growing recently that, in the ultraviolet region, saturated hydrocarbons are not always the inert spectroscopic solvents usually believed. Hastings, Franklin, Schiller, and Matsen [1] originally showed that iodine dissolved in saturated hydrocarbons such as *n*-heptane and *cyclo*hexane has strong absorption below 2600 Å which varies appreciably with the hydrocarbon studied. They assumed that the spectrum in *n*-hexane was characteristic of iodine itself and, by subtracting this from the other measured spectra, obtained what were regarded as charge-transfer spectra of very weak saturated hydrocarbon–iodine complexes, analogous to the well-established aromatic hydrocarbon–iodine complexes.

However, it was shown [2] that this assumption is almost certainly incorrect, since the strong absorption is not found with iodine in the gas phase or dissolved in fully fluorinated solvents (down to 2100 Å), and is present to a much smaller extent with iodine in chloroform. These results, together with measurements in mixed *n*-heptane–perfluoroheptane solutions, made it very unlikely that a solvent shift of the strong *N*–*V* transition (with a maximum at 1750 Å) is involved, and it was concluded that the greater part of the absorption (even with *n*-hexane) is due to a charge-transfer transition. According to a recent accurate determination [3] the ionisation potential of chloroform [3] (11·42 ± 0·03 v) is considerably greater than that of *n*-hexane [4] (10·43 v), which agrees with the above interpretation of the iodine spectra. Bromine behaves similarly to iodine.[5] Oxygen dissolved in saturated hydrocarbons absorbs appreciably below about 2500 Å, and this has again been attributed to charge-transfer transitions.[2,6,7]

There is, however, some uncertainty as to the species responsible for these transitions. By analogy with the large number of well-defined molecular complexes of the donor–acceptor type, it is possible that very weak complexes are involved. Alternatively, it was suggested [2] that a charge-transfer transition might occur during the collision of an iodine molecule with a hydrocarbon molecule, in the absence of any complex formation; this idea was extended by Orgel and Mulliken,[8] who gave theoretical reasons for supposing that a charge-transfer transition can occur between an iodine (or other acceptor) molecule and a hydrocarbon molecule which are merely in contact ("contact charge-transfer spectra"). The absence of any independent evidence for complex formation in these solutions [9,10] agrees with this interpretation.

[1] Hastings, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2900.
[2] Evans, *J. Chem. Phys.*, 1955, **23**, 1424.
[3] Watanabe, *ibid.*, 1957, **26**, 542.
[4] Honig, *ibid.*, 1948, **16**, 105.
[5] Evans, *ibid.*, 1955, **23**, 1426.
[6] Evans, *J.*, 1953, 345.
[7] Munck and Scott, *Nature*, 1956, **177**, 587.
[8] Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845.
[9] Kortüm and Vogel, *Z. Electrochem.*, 1955, **59**, 16.
[10] Jepson and Rowlinson, *J.*, 1956, 1278.

Accordingly, further measurements on the absorption spectrum of iodine in saturated hydrocarbons have been made, at both room and low temperatures. Apart from the usual solvent shift due to changes in the refractive index of the solution, and also a possible sharpening of the bands, little change would be expected in contact charge-transfer spectra on cooling to low temperatures. The interaction of tetranitromethane, another acceptor molecule, with *cyclo*hexane and 2 : 2 : 4-trimethylpentane has also been studied.

Experimental

Materials.—For low-temperature measurements on iodine solutions the saturated hydrocarbons should be as free as possible from impurities such as aromatic compounds and olefins which form complexes with iodine, although the presence of *small* amounts of other saturated hydrocarbons is not objectionable. Commercial pure samples of the hydrocarbons were further purified, either by repeated shaking with fuming sulphuric acid, followed by washing, drying, and fractional distillation, or by passing them through a column of freshly baked silica gel. These procedures gave, for any particular hydrocarbon, products with almost identical absorptions in the region 2100—2500 Å. This absorption is largely, though not entirely, due to the dissolved atmospheric oxygen (cf. Evans [6] and Munck and Scott [7]). *cis*- and *trans*-Decalin (stated purity 99·9%) were further purified with silica gel. In addition, a commercial sample of decalin was treated with both fuming sulphuric acid and silica gel, and analysed by gas chromatography (67% *trans*, 33% *cis*). Tetranitromethane was shaken with dilute alkali, washed, dried, and fractionally distilled under reduced pressure. Nitromethane was dried and fractionally distilled.

Measurements.—A Unicam S.P. 500 spectrophotometer was used. The low-temperature cell is described elsewhere.[11] Solutions were deoxygenated with oxygen-free nitrogen, and corrections applied for the contraction of the solvent on cooling.

The spectra of gaseous tetranitromethane and nitromethane were obtained by placing a drop of the liquid in a 1 cm. stoppered cell contained in a thermostatted cell holder. Equilibrium was attained in 1—2 min., and the concentration of vapour obtained from vapour-pressure data.

Results and Discussion

Iodine Solutions.—Low-temperature studies of iodine dissolved in saturated hydrocarbons are complicated by the possibility of iodine's crystallising from the solutions. Norman and Porter [12] claimed that stable yellow solutions could be obtained at liquid-nitrogen temperatures with concentrations of iodine as high as 10^{-3}M; the yellow colour was tentatively attributed to complex formation between the saturated hydrocarbon (*iso*pentane and methyl*cyclo*hexane) and iodine. Sowden and Davidson,[13] however, were able to obtain clear solutions only at much lower concentrations of iodine (*ca.* 10^{-4}M) and similar results were obtained in the present work (cf. also Ham [14]). It therefore seems likely that Norman and Porter's solvents were appreciably impure. The yellow colour of the very dilute solutions of iodine was attributed by Sowden and Davidson to minute amounts of complex-forming impurities such as benzene, and also to crystallisation. Alternatively, colloidal solutions may be formed. The sudden formation of the yellow colour on cooling the solutions below a certain temperature, and its non-disappearance on heating to an appreciably higher temperature (at which an initially violet solution remains unchanged) support this interpretation. In any case, it is very unlikely that the colour is due to complex formation between the saturated hydrocarbon and the iodine.

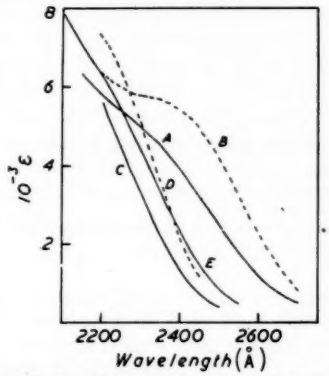
Fortunately, our iodine solutions were stable when cooled to about −130° and, as expected, there was virtually no shift of the 5200 Å visible band. The results obtained in the ultraviolet region for iodine dissolved in methyl*cyclo*hexane, methyl*cyclo*pentane, and 2-methylpentane are shown in Fig. 1. The most marked feature is the appearance of a well-defined shoulder around 2400 Å for methyl*cyclo*hexane at −127°, which can just be detected at room temperature with methyl*cyclo*hexane (and also *cyclo*hexane [1]). Since it

[11] Evans, *J.*, 1957, 4013.
[12] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.
[13] Sowden and Davidson, *J. Amer. Chem. Soc.*, 1956, **78**, 1291.
[14] Ham, *ibid.*, 1954, **76**, 3875.

therefore seemed that a *cyclo*hexane ring had considerably greater donor properties than an open-chain saturated hydrocarbon or *cyclo*pentane ring, the absorption spectrum of iodine dissolved in *cis*- and *trans*-decalin was measured at room temperature (Fig. 2). The effect is even more marked, especially with *cis*-decalin. Although no new band can be detected down to 2200 Å for iodine in 2-methylpentane, one may be present at shorter wavelengths. There is an appreciable red shift of the absorption tail in this case, but the possibility that this is due to a " solvent " shift cannot be excluded.

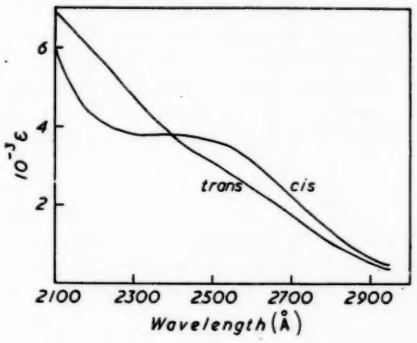
In considering possible explanations for the anomalous behaviour of the *cyclo*hexane ring, it is significant that the ionisation potential of *cyclo*hexane [3] (9·88 ± 0·02 v) is considerably smaller than those of typical open-chain hydrocarbons (*n*-hexane,[4] 10·43 v). Hastings, Franklin, Schiller, and Matsen [1] and McConnell, Ham, and Platt [15] showed that, as expected theoretically, there is a good correlation between the ionisation potential of a donor molecule and the wavelength of the corresponding charge-transfer band with iodine.

FIG. 1. *Absorption spectra of iodine in hydrocarbon solution.*



A, Methyl*cyclo*hexane at *ca.* 22°; *B*, methyl-*cyclo*hexane at −127°; *C*, 2-methylpentane at *ca.* 22°; *D*, 2-methylpentane at −127°; *E*, methyl*cyclo*pentane at *ca.* 22°.

FIG. 2. *Absorption spectra of iodine in* cis- *and* trans-*decalin.*



Steric factors may also play a part, since the shape of a *cyclo*hexane ring will differ appreciably from that of an open-chain hydrocarbon.

The above results are of interest in connection with an effect observed by Ham [14] (during an extensive study of the absorption spectra of iodine complexes at low temperatures) that the charge-transfer bands of certain aromatic compound–iodine complexes showed a very large red shift on cooling to low temperatures in the presence of methyl-*cyclo*hexane (but not 3-methylpentane or *iso*pentane). The shift was apparently due to the appearance of a distinct new band, tentatively attributed to a complex solvated by a methyl*cyclo*hexane molecule.

Freed and Sancier [16] observed a strong charge-transfer peak at 2400 Å for iodine in *cyclo*propane, and pointed out that this is not surprising in view of the similarity in chemical and physical properties between *cyclo*propane and olefins.[17]

As regards the original question of complex formation *versus* " contact charge-transfer spectra," although no definite conclusions can be drawn from our results it seems most likely that while a charge-transfer transition can result from two molecules merely in contact, certain configurations will be more stable thermodynamically than others, and

[15] Ham, Platt, and McConnell, *J. Chem. Phys.*, 1951, **19**, 1301.
[16] Freed and Sancier, *J. Amer. Chem. Soc.*, 1952, **74**, 1273.
[17] " Chemistry of Carbon Compounds," ed. Rodd, Elsevier, 1953, p. 27.

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these will be increasingly favoured at lower temperatures. Some such stable configuration is presumably responsible for the new bands with *cyclo*hexane-type solvents. The residual absorption down to about 2100 Å, and most of the absorption with open-chain hydrocarbons, is probably largely due to contact charge-transfer spectra from random non-specific iodine–hydrocarbon configurations.

Charge-transfer Spectra with Tetranitromethane.—Charge-transfer spectra involving saturated hydrocarbons should clearly not be restricted to iodine, bromine, and oxygen. Unfortunately the great majority of other electron-accepting molecules show very strong absorption below about 2700 Å which would tend to obscure any charge-transfer band. However tetranitromethane, which gives charge-transfer spectra extending into the visible region with aromatic and olefinic molecules,[18] does not absorb very strongly above 2400 Å, and accordingly its spectrum was measured in the vapour phase and in *iso*octane and *cyclo*hexane solution. Both tetranitromethane and nitromethane have a very weak absorption maximum in the vapour phase at 2750 Å,[19,20] which indicates that there is little interaction between the nitro-groups in the former. (This spectral similarity also extends to shorter wavelengths.) The spectrum of nitromethane was therefore measured

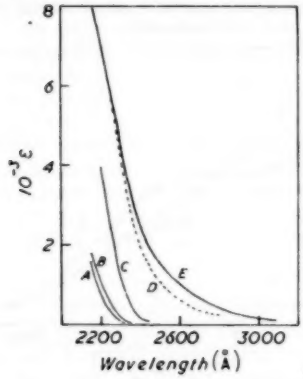

FIG. 3. *Absorption spectra of electron acceptors.*
A, Nitromethane vapour.
B, Nitromethane in *cyclo*hexane.
C, Tetranitromethane vapour.
D, Tetranitromethane in 2 : 2 : 4-trimethylpentane.
E, Tetranitromethane in *cyclo*hexane.

under similar conditions for comparison, since although any solvent shift should be similar to that with tetranitromethane, no charge-transfer band would be expected.

The results are shown in Fig. 3. Only a small (solvent) shift is observed for nitromethane, but with tetranitromethane the absorption at longer wavelengths is very much greater in *iso*octane and (especially) *cyclo*hexane than in the vapour phase. We have little doubt that this additional absorption is due to charge-transfer transitions, probably largely "contact charge-transfer spectra." These results for tetranitromethane are therefore consistent with the interpretation given for the iodine spectra. The ultraviolet absorption of tetranitromethane in aqueous solution has been measured by Kortüm;[21] his results resemble the vapour spectrum much more closely than the spectra obtained in *iso*octane or *cyclo*hexane solution. This is not unexpected in view of the very high ionisation potential of water (12·59 ± 0·01 v).

I thank the University of Oxford for an Imperial Chemical Industries Limited Research Fellowship, Dr. R. E. Richards for the *cis*- and *trans*-decalin, and Dr. I. Scott for gas chromatograms.

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[*Received, June 4th*, 1957.]

[18] Werner, *Ber.*, 1909, **42**, 4342; Heilbronner, *Helv. Chim. Acta*, 1953, **36**, 1121.
[19] Nicholson, *J.*, 1949, 1553.
[20] Haszeldine, *J.*, 1953, 2525.
[21] Kortüm, *Z. phys. Chem.*, 1939, **43**, *B*, 271.

850. *Solutions in Sulphuric Acid. Part XXIII.* Cryoscopic Measurements on Nitrobenzene and the Nitrotoluenes.*

By R. J. Gillespie and E. A. Robinson.

Cryoscopic measurements on nitrobenzene and the nitrotoluenes in 100% sulphuric acid give more accurate values of the basic dissociation constants of these compounds than those obtained earlier with slightly aqueous sulphuric acid as solvent. It is suggested that nitro-compounds in general give abnormally high freezing points in slightly aqueous sulphuric acid and a possible explanation is given.

A number of aromatic mononitro-compounds have been shown to behave as weak bases in sulphuric acid by means of cryoscopy,[1,2] conductimetry,[2] and spectroscopy.[3] The results of these different methods are in good quantitative agreement, except for some early measurements[1] carried out in slightly aqueous sulphuric acid, which gave higher values of the basic ionisation constants than the other methods. Brayford and Wyatt[4] found that polynitro-compounds, which are non-electrolytes, give abnormally high freezing-point depressions in slightly aqueous sulphuric acid. These results were attributed to salting-out of the nitro-compound by the electrolyte hydroxonium hydrogen sulphate. Gillespie and Solomons[2] suggested that, in the case of mononitro-compounds, the un-ionised portion might show the same behaviour, thus giving abnormally high overall freezing-point depressions and hence high basic dissociation constants. New cryoscopic measurements have therefore been made in 100% sulphuric acid to test this suggestion.

Experimental

Apparatus.—The apparatus and general procedure for making the cryoscopic and conductimetric measurements have been described.[5,6] Freezing points were measured with a solid-stem mercury-in-glass thermometer which was periodically calibrated against a platinum resistance thermometer.

Materials.—Sulphuric acid, prepared as previously described,[7] was adjusted to maximum freezing point before each experiment. Liquid solutes were dried and redistilled: nitrobenzene, b. p. 209°, n_D^{25} 1·550; *o*-nitrotoluene, b. p. 218°, n_D^{25} 1·543; *m*-nitrotoluene, b. p. 228°, n_D^{25} 1·544. *p*-Nitrotoluene, recrystallised from alcohol, had m. p. 54°.

Calculations.—The freezing-point depression θ is related to the molality of the solute m_2 by eqn. (2) of Part XIX,[8] *i.e.*,

$$\theta/m_2 = 6{\cdot}12\nu'(1 - 0{\cdot}001950\theta)[1 + (2s_2 - \nu')m_2/2m_1]$$

where ν' is approximately equal to ν, the number of moles of ions and molecules which are formed by one molecule of the solute, and the other symbols have the meanings given previously.[7] For a weak base, $B + H_2SO_4 \rightleftharpoons BH^+ + HSO_4^-$, we have $\alpha = \nu - 1$, where α is the degree of ionisation and the basic dissociation constant $K_b = [BH^+][HSO_4^-]/[B] = (\nu - 1)[HSO_4^-]/(2 - \nu)$, where $[HSO_4^-]$ is the *total* concentration of hydrogen sulphate ion, including that remaining from the incompletely repressed autoprotolysis of the solvent ($K_{ap} = 1{\cdot}56 \times 10^{-4}$ mole^2 kg.$^{-2}$).

Results.—For convenience the freezing points for two experiments on each solute, in each of

* Part XXII, *J.*, 1957, 1804.

[1] Gillespie, *J.*, 1950, 2542.
[2] Gillespie and Solomons, *J.*, 1957, 1796.
[3] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[4] Brayford and Wyatt, *J.*, 1955, 3453.
[5] Gillespie, *J.*, 1950, 2473.
[6] Gillespie, Oubridge, and Solomons, *J.*, 1957, 1804.
[7] Gillespie and Oubridge, *J.*, 1956, 80.
[8] Flowers, Gillespie, and Oubridge, *J.*, 1956, 1925.

which an average of six separate additions of solute were made, were plotted on a large scale, and freezing points of the solutions at round concentrations interpolated. These interpolated freezing points (column 2, Table 1), after correction for the depression produced by the ions remaining from the incompletely repressed autoprotolysis of the solvent, are given in column 3 of Table 1. Values of the freezing-point depression θ, calculated from the corrected freezing points, are given in column 4 of Table 1, which also includes values of ν′ and K_b.

TABLE 1. *Results of the cryoscopic measurements.*

	Nitrobenzene						m-*Nitrotoluene*					
m_2	F. p. obs.	F. p. corr.	θ	ν′	10^3K_b		m_2	F. p. obs.	F. p. corr.	θ	ν′	10^3K_b	
0·000	10·365°	10·515°	—	—			0·000	10·365°	10·515°	—	—		
0·050	10·026	10·108	0·407°	1·33	1·1		0·050	9·976	10·033	0·482°	1·57	(3·8)	
0·100	9·682	9·742	0·773	1·26	1·1		0·100	9·628	9·679	0·854	1·39	2·5	
0·150	9·344	9·392	1·123	1·22	1·0	1·1	0·150	9·284	9·322	1·193	1·30	2·1	2·0
0·200	9·003	9·045	1·470	1·20	1·0		0·200	8·936	8·967	1·548	1·27	2·0	
0·250	8·668	8·706	1·809	1·18	1·1		0·250	8·588	8·616	1·899	1·24	1·9	
0·300	8·320	8·355	2·160	1·17	1·1		0·300	8·242	8·268	2·247	1·21	1·6	
	o-*Nitrotoluene*						p-*Nitrotoluene*					
0·000	10·365	10·515	—	—			0·000	10·365	10·515	—	—		
0·050	9·954	10·000	0·515	1·68	(8·0)		0·050	9·940	9·982	0·533	1·74	(11·5)	
0·100	9·552	9·584	0·931	1·52	5·9		0·100	9·520	9·547	0·973	1·60	9·3	
0·150	9·152	9·177	1·338	1·45	5·7		0·150	9·096	9·118	1·397	1·52	9·0	9·4
0·200	8·752	8·773	1·742	1·42	6·1	6·2	0·200	8·674	8·693	1·822	1·49	9·5	
0·250	8·356	8·375	2·140	1·40	6·7		0·250	8·252	8·269	2·246	1·46	9·8	
0·300	7·984	8·001	2·514	1·37	6·6								

DISCUSSION

The mean values of the basic dissociation constants K_b given in Table 1 are compared in Table 2 with earlier values [1] obtained in slightly aqueous sulphuric acid. The new values are appreciably lower than earlier ones and are in good agreement with values obtained by other methods. Thus the present results substantiate Gillespie and Solomons's suggestion [2] that mononitro-compounds, like polynitro-compounds, give

TABLE 2. *Dissociation constants of some nitro-compounds.*

	Cryoscopic			
	100% H_2SO_4	Slightly aqueous H_2SO_4	Conduct.	Spectr.
Nitrobenzene	0·011	0·025	0·010	0·009
o-Nitrotoluene	0·062	—	0·067	—
m-Nitrotoluene	0·020	—	0·023	0·024
p-Nitrotoluene	0·094	0·17	0·095	0·077
p-Chloronitrobenzene	0·003[3]	—	0·004	0·0046

abnormally large freezing-point depressions in slightly aqueous sulphuric acid. A probable explanation is that the un-ionised part of the nitro-compound is salted out [4] by the electrolyte H_3O^+,HSO_4^-. Our results show that accurate values of the basic dissociation constants of mononitro-compounds can be obtained cryoscopically in 100% sulphuric acid but not in slightly aqueous sulphuric acid.

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851. *Free Radicals and Radical Stability. Part XIII.* Triphenylmethyls containing* m-*Methoxyl Substituents.*

By S. T. Bowden.

The discrepancy between the values of the radical stability determined by the cryoscopic and the magnetic-susceptibility methods is discussed. The former method shows that the stability of (*m*-methoxyphenyl)diphenylmethyl is lower than that of the *ortho*- and the *para*-substituted radical. The presence of more than one substituent leads to clashing influences, and diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl has practically the same stability as (3 : 4-dimethoxyphenyl)diphenylmethyl. The dissociation of triphenylmethyl iodide is also favoured by the presence of methoxyl substituents.

The methoxyl-substituted radicals give a higher yield of peroxide than does triphenylmethyl. In the reaction between a (methoxyphenyl)diphenylmethyl chloride and phenylmagnesium bromide the yield of the tetraphenylmethane is lower for the *meta*-substituted than for the *ortho*-substituted derivative where the effect of steric hindrance would be greater.

The influence of methoxyl substituents in the *ortho*- and *para*-positions of triphenylmethyl has been studied by Gomberg and Nishida,[1] Gomberg and Buchler,[2] Lund,[3] and more recently Marvel, Whitson, and Johnston [4] who confined their study to the effect of orientation on the dissociation of the corresponding hexa-arylethanes. The present work was undertaken to examine primarily the influence of *meta*-substitution by methoxyl on the properties of the free radicals and their saturated derivatives.

The annexed Table shows that the values of the degree of dissociation determined by the cryoscopic method differ considerably from those found by the magnetic-susceptibility method. In discussing these discrepancies Marvel and his co-workers [4] state: "All of the methoxyl substituted hexa-arylethanes were found to be relatively unstable, and the change in magnetic susceptibility with the age of the solution showed that these radicals decompose quickly. The molecular-weight determinations undoubtedly show too high values for the radical because of the presence of disproportionation products in the aged solutions of the ethanes." In so far as the chemical stability of the radical solutions is

Methoxyl-substituted hexaphenylethanes.

Free radical	Dissociation of the ethane (%) Cryoscopic method	Magnetic method
(*o*-Methoxyphenyl)diphenylmethyl	26 (Gomberg and Nishida)	3·8 (Marvel *et al.*)
(*m*-Methoxyphenyl)diphenylmethyl	15 (Present work)	2·6 ,,
(*p*-Methoxyphenyl)diphenylmethyl	24 (Gomberg and Buchler)	4·4 ,,
Di-(*o*-methoxyphenyl)phenylmethyl	40 (Bowden)	7·3 ,,
Tri-(*o*-methoxyphenyl)methyl	100 (Lund)	42 ,,
Tri-(*m*-methoxyphenyl)methyl	13 (Present work)	8·5 ,,
Diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl ...	23 ,,	—

concerned, the experience of these investigators is at variance with that of other workers. When prepared under conditions which preclude oxidation and photodecomposition and minimise disproportionation and isomerisation, these triphenylmethyls are among the most stable substituted radicals which have yet been prepared. Far from decomposing quickly the radicals prepared in Gomberg's laboratory and at Cardiff exhibited little tendency to undergo these reactions at room temperature, and were kept in the dark for many hours or even days without substantial change. No significant amounts of decomposition products were formed during two hours required for the cryoscopic measurements

* Part XII, *J.*, 1940, 1249.

[1] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1922, **45**, 190.
[2] Gomberg and Buchler, *ibid.*, p. 207.
[3] Lund, *ibid.*, 1927, **49**, 1346.
[4] Marvel, Whitson, and Johnston, *ibid.*, 1944, **66**, 415.

since the volume of oxygen absorbed by the radical system at the end of this period seldom differed by more than 1% from the nearly theoretical value found for the fresh radical. Moreover, the yield of triarylmethyl peroxide obtained by oxidation of the solution after completion of the cryoscopic determinations corresponded closely to that found for the fresh solution. Further, most of the hexaphenylethanes were isolated in the solid state.

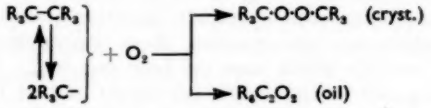
Although the low values of dissociation reported by Marvel and his co-workers [4] may be due to isomerization, leading to derivatives analogous to *p*-diphenylmethyltetraphenylmethane, they probably arise from an inherent defect in the application of the magnetic-susceptibility method to determine the concentration of free radical in solution. In a critical study of the method Selwood and Dobres [5] point out that their own results with triarylmethyl systems can be explained on the basis of an underestimation in the diamagnetic correction of 65—120% and an increase of 195—300% in the principal molecular susceptibility normal to the plane of the rings. These values are large, and there is no means of estimating the electronic currents in the resonating bonds attaching the aryl nuclei to the methyl-carbon atom. There is no doubt that the published values of the radical stability are far too low, and until the difficulties inherent in the magnetic-susceptibility method are resolved we prefer to rely on the simpler and more direct cryoscopic method. According to Marvel and his co-workers,[4] steric factors are responsible for the high unimolecular stability of triphenylmethyls containing *o*-methyl or *o*-methoxyl groups. This conclusion, however, is based solely on the questionable data furnished by the magnetic-susceptibility method. Although steric influences may operate to some extent in preventing association of the radical to the ethane or in lengthening the central C–C bond,[6] the cryoscopic results indicate that these effects are small with substituents such

(Methoxyphenyl)diphenylmethyls.

Radical	M. p. (decomp.) of the ethane	Dissociation of the ethane (%)	Colour of solution	Absorption of O_2 (%) *	Absorption of I_2 (%) *
Triphenylmethyl	145°	2—4	Yellow	99·9	80
(*o*-Methoxyphenyl)diphenylmethyl	117—121	26	Yellow-brown	93·6	64
(*m*-Methoxyphenyl)diphenylmethyl	120—124	16	Orange-yellow	99·1	60
(*p*-Methoxyphenyl)diphenylmethyl	145—150	24	Orange-yellow	100·9	60

* Of theoretical.

as methyl and methoxyl. If we refer the greater unimolecular stability of the substituted radicals to the increase in degeneracy arising from the modification of the inductive and mesomeric effects,[7] we would expect the stability of (*m*-methoxyphenyl)diphenylmethyl to be higher than that of triphenylmethyl but lower than that of the *o*- and *p*-derivatives. This is substantiated by the annexed cryoscopic results. In other respects (*m*-methoxyphenyl)diphenylmethyl is similar to the *o*- and *p*-derivatives. It absorbs rapidly a mole of oxygen with complete decolorization of the solution. The oxidation of a triarylmethyl radical generally involves the formation of a crystalline peroxide and an oily, isomeric product:



and it is evident that the first reaction is favoured by the presence of the methoxyl group since the yield of peroxide is 15% higher than that of triphenylmethyl peroxide. The radical also combines with iodine until an equilibrium is established, and, as might be expected on the basis of the behaviour of the corresponding ethanes, the degree of

[5] Selwood and Dobres, *J. Amer. Chem. Soc.*, 1950, **72**, 3860.
[6] Ziegler, *Annalen*, 1942, **551**, 127.
[7] Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421; *Trans. Faraday Soc.*, 1934 **30**, 52.

dissociation of the three (methoxyphenyl)diphenylmethyl iodides in benzene at room temperature is substantially higher than that of triphenylmethyl iodide.

The influence of methoxyl substituents on the stability of a triarylmethyl is not additive, and it is not possible to predict its value from a knowledge of the number and orientation of the substituents. The stability of di-(*o*-methoxyphenyl)phenylmethyl is 40% but the stabilities of the 2 : 4- and the 3 : 4-derivative are 29% and 12%, respectively. Although tri-(*o*-methoxyphenyl)methyl is reported to be almost completely unimolecular in solution,[3] the present results indicate that the stability of the corresponding tri-*meta*-derivative differs little from that of the monosubstituted radical. The same inhibitory influence of *meta*-substituents is apparent in the radical diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl with a stability of 23%, which does not differ appreciably from that of (3 : 4-dimethoxyphenyl)diphenylmethyl.

The difficulty experienced in synthesizing tetraphenylmethane is generally ascribed to steric hindrance,[8] and the hydrocarbon is formed in only 2—5% yield by the action of phenylmagnesium bromide on triphenylmethyl chloride. In the analogous reaction between the Grignard reagent and (*m*-methoxyphenyl)diphenylmethyl chloride we find that the yield of (*m*-methoxyphenyl)triphenylmethane is 20%, which is lower, however, than the yield of (*o*-methoxyphenyl)triphenylmethane in whose formation steric hindrance would be expected to be more strongly operative.

Experimental

(m-*Methoxyphenyl*)*diphenylmethanol*.—The compound was prepared in 50% yield from *m*-methoxyphenylmagnesium iodide or bromide and benzophenone, but was more conveniently obtained from phenylmagnesium bromide and methyl or ethyl *p*-anisate.[9,4] Recrystallized from alcohol or ether, it melted at 88°.

Treatment of a cold solution of the alcohol in acetic anhydride with slight excess of 70% perchloric acid gave deep violet crystals of the *perchlorate*, m. p. 110° (Found: ClO_4, 26·5. $C_{20}H_{17}O_5Cl$ requires ClO_4, 26·7%).

(m-*Methoxyphenyl*)*diphenylmethane*.—The alcohol (1 g.), glacial acetic acid (15 c.c.), and zinc dust (1 g.) were heated on the steam-bath for 3 hr. On concentration of the filtered solution the methane (0·7 g.) was deposited, and having m. p. 86° (from alcohol), not changed on admixture with a specimen prepared by reduction of the alcohol with formic acid.[10]

(m-*Methoxyphenyl*)*diphenylmethyl Chloride*.—(*a*) The compound was prepared by Marvel *et al.*[4] by refluxing a benzene solution of the alcohol with excess of acetyl chloride for several hours, and had m. p. 89—90° after recrystallisation from ethyl acetate. Since the alcohol reacts rapidly with acetyl chloride in ether–light petroleum, we adopted the following procedure. Acetyl chloride (0·25 mole) was added to a solution of the alcohol (0·1 mole in 1 : 1 ether–light petroleum), and the mixture was simmered gently for 15 min. (*m*-Methoxyphenyl)diphenylmethyl chloride was slowly deposited on storage in the cold, and had m. p. 88° after recrystallization from the same solvent mixture.

(*b*) A 10% solution of the alcohol in ether was saturated with hydrogen chloride and kept over calcium chloride in a stoppered vessel for 24 hr. The filtered solution was concentrated to one-third of its bulk, and the deposited (*m*-methoxyphenyl)diphenylmethyl chloride was filtered off in a stream of dry air. Recrystallized from ether–light petroleum, the compound had m. p. 88° (mixed m. p. with the alcohol, 75—76°) (Found: Cl, 11·4. Calc. for $C_{20}H_{17}OCl$: Cl, 11·5%). This method does not yield such a readily purified product as method (*a*).

(m-*Methoxyphenyl*)*triphenylmethane*.—A filtered solution of phenylmagnesium bromide [from bromobenzene (9·0 g.) and magnesium (1·4 g.)], boiling under nitrogen, was treated with (*m*-methoxyphenyl)diphenylmethyl chloride (5·0 g.) during 1 hr. After 12 hours' heating the cooled solution was acidified and treated with steam to remove volatile material. The solid residue was washed with water, dried, dissolved in the minimum amount of benzene, treated with an equal volume of light petroleum, and kept for several days. The deposited (*m*-methoxyphenyl)triphenylmethane (20·4%) was obtained colourless after two recrystallizations from

[8] Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1144.
[9] Baeyer and Villiger, *Annalen*, 1907, **354**, 171.
[10] Kauffmann and Panwitz, *Ber.*, 1912, **45**, 770.

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glacial acetic acid, and had m. p. 163° [Found: C, 88·9; H, 6·5%; *M* (Rast), 346. $C_{26}H_{22}O$ requires C, 89·1; H, 6·3%; *M*, 350].

(m-*Methoxyphenyl*)*diphenylmethyl.*—The free radical was prepared by agitating a 10% benzene solution of the chloride with rigorously dried molecular silver under carbon dioxide with exclusion of light. The yellow solution was transferred into the standard type of isolation apparatus,[11] and the solvent removed at 45°, the pressure being finally reduced to 20 mm. The residual oil was dissolved in the minimum amount of warm acetone, and cooled to −10°. Di-*m*-methoxyhexaphenylethane was deposited as very pale yellow crystals, which were washed with small amounts of cold light petroleum and then dried *in situ* at 50° in a stream of carbon dioxide; it had m. p. (in vacuum) 120—124° (decomp.).

The volume of 0·99 mol. of oxygen was absorbed by bromobenzene solutions. The benzene solution rapidly absorbed iodine to form (*m*-methoxyphenyl)diphenylmethyl iodide, and at 18° equilibrium was established when the amount of combined iodine corresponded to 60% of the theoretical value.

(m-*Methoxyphenyl*)*diphenylmethyl Peroxide.*—Marvel *et al.*[4] give no preparative details, but state that the compound has m. p. 156—157°. We prepared the compound by passing air through a 10% ethereal solution of the radical until the colour was discharged and the peroxide was precipitated, or by allowing a benzene solution of the radical to evaporate spontaneously in the air, and then triturating the residue with ether and light petroleum. The solid was recrystallized from 1 : 1 benzene–ligroin, or by dissolving the compound in xylene at 50° and rapidly cooling the solution to 0°. It was thus obtained as a colourless powder, m. p. 163° (Found: C, 82·8; H, 6·0. Calc. for $C_{40}H_{34}O_4$: C, 83·2; H, 5·9%). The average yield (85%) is substantially higher than that found for triphenylmethyl peroxide (70%).

Tri-(m-*methoxyphenyl*)*methanol.*—The compound, m. p. 119·5° (from alcohol) (cf. ref. 9), was obtained in 48% yield from *m*-methoxyphenylmagnesium iodide and methyl *m*-anisate.

Tri-(m-*methoxyphenyl*)*methane.*—A 10% solution of the alcohol in glacial acetic acid was boiled with zinc dust for 6 hr. Addition of water to the filtered solution precipitated the *methane*, which after three recrystallizations from alcohol melted at 103° (Found: C, 78·7; H, 6·7. $C_{22}H_{22}O_3$ requires C, 79·0; H, 6·6%).

Tri-(m-*methoxyphenyl*)*methyl Chloride.*—Marvel *et al.*[4] prepared the compound by prolonged boiling of a benzene solution of the alcohol with excess of acetyl chloride, but a cleaner product was obtained by the following method. A 15% solution of the alcohol in ether at 0° was saturated with hydrogen chloride, and set aside for 12 hr. in a stoppered vessel with a glass basket containing fused calcium chloride immersed in the liquid. The trimethoxytriphenylmethyl chloride was deposited as a colourless solid which melted at 123—124° after recrystallization from 1 : 1 benzene–ether (Found: Cl, 9·6. Calc. for $C_{22}H_{21}O_3Cl$: Cl, 9·6%).

Tri-(m-*methoxyphenyl*)*methyl.*—Agitation of the chloride (1 g.) in bromobenzene (10 ml.) with 5 times the theoretical amount of molecular silver led to complete reduction in 20 min. at room temperature with formation of a yellowish-red solution. Removal of the solvent from a 15% benzene solution of the radical in the isolation apparatus gave the ethane as a yellowish-red oil which did not crystallize.

A freshly prepared solution of the radical absorbed 0·98 mol. of oxygen in 5 min., and 0·97 mol. in the dark in 2 hr. There was a further absorption of a similar amount in 8 days owing to further oxidation. The *peroxide* was isolated by passing air through a 15% benzene solution of the radical until most of the solvent was removed, triturating the residue with light petroleum, and rapidly recrystallizing the product from benzene under carbon dioxide. It had m. p. 153—154° whereas Marvel *et al.*[4] found m. p. 155—156° (Found: C, 75·4; H, 6·1. Calc. for $C_{44}H_{42}O_8$: C, 75·6; H, 6·1%).

Diphenyl-(3 : 4 : 5-*trimethoxyphenyl*)*methyl Chloride.*—The compound was prepared by a modification of Bogert and Isham's method.[12] A suspension of diphenyl(3 : 4 : 5-trimethoxyphenyl)methanol (5 g.) in ether (50 ml.) containing a few lumps of calcium chloride was saturated with hydrogen chloride. After 12 hr. the deep red solution was filtered and concentrated to one-third of its bulk in a dry atmosphere. The chloride deposited on cooling had m. p. 110° after recrystallisation from ether. The *ferric chloride addition compound* was obtained as a dark red precipitate on mixing ethereal solutions of the components. After being washed with ether

[11] Gomberg and Schoepfle, *J. Amer. Chem. Soc.*, 1917, **39**, 1659.
[12] Bogert and Isham, *ibid.*, 1914, **36**, 514.

and kept over soda-lime and silica gel in an evacuated desiccator, it had m. p. 140° (Found: Cl, 29·4. $C_{22}H_{21}O_3Cl,FeCl_3$ requires Cl, 29·3%). The addition compounds with zinc and mercuric chlorides were dark red oils.

Diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl.—The solvent was removed from a 15% solution of the radical in benzene in the isolation apparatus, at 45° under reduced pressure in a stream of carbon dioxide. The residual orange-yellow oil, when dissolved in the minimum amount 1 : 4 acetone–light petroleum and cooled to −10°, deposited the pale yellow ethane, m. p. 154—155° (decomp.; vac.). In liquid sulphur dioxide and dimethyl sulphate it formed crimson solutions. It rapidly absorbed 0·96 mol. of oxygen in non-ionizing solvents, but some yellow colour remained; further slow absorption took place.

Diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl Peroxide.—A 10% solution of diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl chloride was shaken with a large excess of mercury in a sealed tube for 4 hr. in the dark. Air was passed through the filtered solution for 20 min. The *peroxide* was precipitated as a yellow powder, and was obtained as colourless crystals, m. p. 175°, by rapid recrystallization from hot benzene (Found: C, 75·5; H, 6·1. $C_{44}H_{42}O_8$ requires C, 75·6; H, 6·1%).

Dissociation of the Ethanes.—The degree of dissociation was determined by the indirect cryoscopic method with the customary precautions to avoid isomerization, disproportionation, and oxidation during the preparation of the radical and the subsequent measurements.[13] The solvent employed was benzene; *K*, 52·5°.

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	*M*	Dissocn. of ethane (%)
	(m-*Methoxyphenyl*)*diphenylmethyl.*				
M of radical = 273·3; *M* of the ethane = 546·5.					
18·10	0·3080	0·2726	0·166°	478·9	14·1
	0·5570	0·4930	0·302	476·1	14·8
	0·7429	0·6573	0·405	469·7	16·4
18·11	0·2882	0·2549	0·156	474·0	15·3
	0·4483	0·4259	0·266	466·0	17·3
	0·7460	0·6894	0·420	476·2	14·7
	0·8204	0·7552	0·460	475·8	14·9
18·10	0·2548	0·2255	0·139	470·6	16·1
	0·5038	0·4459	0·279	463·6	17·7
	0·6908	0·6114	0·377	470·3	16·0
	0·7740	0·6850	0·420	473·2	15·5
18·47	0·4373	0·3871	0·231	476·6	14·7
	0·6304	0·5580	0·268	470·2	16·0
	0·7838	0·6938	0·327	479·2	14·1
	Diphenyl-(3 : 4 : 5-trimethoxyphenyl)methyl.				
M of radical = 333·3; *M* of the ethane = 666·6.					
18·13	0·2604	0·2351	0·125	544·6	22·2
	0·5238	0·4730	0·259	528·8	26·0
	0·7409	0·6691	0·363	538·8	23·0
	0·8941	0·8074	0·441	530·8	23·7
18·47	0·2536	0·2290	0·123	529·3	25·2
	0·4421	0·3992	0·210	540·5	22·6
	0·6634	0·5991	0·313	544·3	21·7
18·47	0·2724	0·2460	0·131	538·8	24·8
	0·4794	0·4329	0·226	544·6	22·5
	0·6966	0·6290	0·328	546·3	21·9

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	*M*	Dissocn. of ethane (%)
	Tri-(m-*methoxyphenyl*)*methyl.*				
M of radical = 333·3; *M* of the ethane = 666·6.					
18·10	0·1970	0·1780	0·089°	580·3	14·8
	0·4304	0·3890	0·188	600·1	11·1
	0·6993	0·6320	0·308	597·8	11·5
18·10	0·2379	0·2150	0·107	582·8	14·4
	0·7767	0·7020	0·333	602·4	10·7
18·10	0·4769	0·4309	0·209	598·2	11·4
	0·6662	0·6020	0·290	604·9	10·2
18·48	0·5987	0·5411	0·265	580·3	14·9
	0·8212	0·7420	0·356	592·3	12·5
18·48	0·6407	0·5790	0·279	589·6	13·1
21·10	1·018	0·9196	0·412	583·3	14·3

After each set of determinations, the solution was quickly filtered from silver and silver chloride, and the radical converted into peroxide by passing air through the solution or allowing the latter to evaporate in the atmosphere. The yield of peroxide was practically the same as that obtained by oxidation of the freshly prepared solutions.

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[*Received, February 28th,* 1957.]

[13] Bowden, *J.*, 1939, 37.

852. *Free Radicals and Radical Stability. Part XIV.*[1] *(Ethoxyphenyl)diphenylmethanols and the Free Radical (o-Ethoxyphenyl)diphenylmethyl.*

By S. T. Bowden and D. T. Zalichi.

The basicity of triphenylmethanol is increased slightly more by the ethoxyl than by the methoxyl group.

Disproportionation of (*o*-ethoxyphenyl)diphenylmethyl in benzene is slow at room temperature, and the solid ethane can be isolated. Cryoscopic measurements show that the ethoxyl substituent promotes dissociation of the ethane slightly less than methoxyl does. In benzene at room temperature (*o*-ethoxyphenyl)diphenylmethyl iodide is dissociated to the same extent as the methoxyl derivative.

The (ethoxyphenyl)diphenylmethanols were prepared for comparison of their basicities and of the salts with the corresponding methoxyl derivatives.[1-3] The introduction of a methoxyl group into triphenylmethanol increases the basicity, and generally leads to a bathochromic shift in the absorption spectrum of the sulphate, but these effects are slightly more marked with ethoxyl (see Table, where the basicity values are referred to that of triphenylmethanol as unity). The halochromic effect of the alkoxyl group is greatest for *ortho*-substitution, whereas the basicity change is greatest for *para*-substitution and least for *meta*-substitution. There is no simple connection between the resistance of the salt to hydrolysis as expressed by the basicity, and the optical properties of the system.

Basicity and halochromism.

Diphenylmethanol	Basicity	Colour of sulphate	Diphenylmethanol	Basicity	Colour of sulphate
(*o*-Methoxyphenyl)- ...	2·0	Red	(*o*-Ethoxyphenyl)- ...	2·3	Red
(*m*-Methoxyphenyl)- ...	1·2	Orange-red	(*m*-Ethoxyphenyl)- ...	2·0	Reddish-brown
(*p*-Methoxyphenyl)- ...	6·5	Red	(*p*-Ethoxyphenyl)- ...	7·9	Orange-brown

In the thermal decomposition of formic acid solutions of (*o*-methoxyphenyl)diphenylmethanol at 77° the evolution of carbon dioxide is more rapid and more nearly approaches the theoretical value than for similar solutions of triphenylmethanol, and the favourable influence of *o*-methoxyl is further shown by the higher yield of triarylmethane.[4] The behaviour of the solution of (*o*-ethoxyphenyl)diphenylmethanol, however, differs markedly from that of the *o*-methoxyl derivative inasmuch as the reaction is more rapid in the initial stages, but slows down sharply when about 0·3 mol. of the gas has been evolved: the colour of the (*o*-ethoxyphenyl)diphenylmethyl cation is discharged and the solution becomes brown, whereas solutions of the corresponding ions of triphenylmethyl and (*o*-methoxyphenyl)diphenylmethyl become colourless. The overall inhibiting influence of the ethoxyl substituent on the reduction process arises from secondary reactions which lead to coloured products without liberation of carbon dioxide. Although (*p*-ethoxyphenyl)diphenylmethane may be isolated from the solution, the compound is more readily prepared by reduction of the alcohol with zinc and acetic acid.

(*o*-Ethoxyphenyl)diphenylmethyl chloride dissolves in non-ionizing solvents to form colourless solutions, and is reduced to the free radical by mercury or silver. In bromobenzene solution at 18° reduction by molecular silver is slower than that of triphenylmethyl chloride. A 2% solution of (*o*-ethoxyphenyl)diphenylmethyl in benzene is yellowish-red, and there is no appreciable change of colour in 4 days in the dark. The radical rapidly absorbs 0·95 mol. of oxygen, and forms a normal peroxide. Although the

[1] Part XIII, preceding paper.
[2] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1922, **45**, 190.
[3] Gomberg and Buchler, *ibid.*, p. 207.
[4] Part VIII, *J.*, 1940, 874.

radical is much more prone to disproportionate and/or isomerize than triphenylmethyl, these reactions are slow at room temperature—solutions which are 24 hr. old absorb practically the same amount of oxygen as the freshly prepared solution.

Di-(*o*-ethoxyphenyl)tetraphenylethane in 2% benzene solution at the freezing point is about 20% dissociated, which is slightly less than for the methoxyl derivative.[1] The ethane, which may be isolated in the solid state from acetone solution, dissolves in organic solvents to yield the characteristic colour of the radical, but forms a red solution in liquid sulphur dioxide owing to ionization. Solutions of the free radical absorb iodine until an equilibrium is established with (*o*-ethoxyphenyl)diphenylmethyl iodide. In benzene at 15° the amount of halogen absorbed is only slightly lower than for the *o*-methoxyl derivative.

Experimental

(p-*Ethoxyphenyl*)*diphenylmethanol*.—Hydrolysis of the interaction product of *p*-phenetylmagnesium bromide and benzophenone gave the alcohol as an oil which, however, was obtained crystalline as follows. Ethereal *p*-ethoxybenzophenone [5] (0·1 mole) was added slowly to a filtered solution of phenylmagnesium bromide (0·1 mole) and, after reaction had completely subsided, the mixture was heated under reflux for 30 min. under a soda-lime guard-tube. The mixture was hydrolysed and acidified with sulphuric acid, and the ethereal layer was washed and dried (Na_2SO_4). The oil obtained on evaporation solidified after prolonged trituration with light petroleum. Recrystallization from 1 : 4 ether–light petroleum gave the colourless *alcohol*, m. p. 54° (Found: C, 82·4; H, 6·8. $C_{21}H_{20}O_2$ requires C, 82·9; H, 6·6%).

(*p*-Ethoxyphenyl)diphenylmethane, previously obtained from (*p*-ethoxyphenyl)diphenylmethyl ethyl ether [6] and from (*p*-hydroxyphenyl)diphenylmethane,[7] was prepared by heating the alcohol (2 g.) with acetic acid (25 ml.) and zinc dust (7 g.) under reflux for 2 hr. The mixture was filtered while hot, and the yellow oil, which was deposited on cooling, was separated and triturated with ligroin until it solidified. Recrystallized from alcohol, the methane was obtained colourless, with m. p. 68° (Found: C, 87·0; H, 6·6. Calc. for $C_{21}H_{20}O$: C, 87·5; H, 7·0%).

(m-*Ethoxyphenyl*)*diphenylmethanol*.—To a filtered solution of phenylmagnesium bromide (0·22 mole) ethereal ethyl *m*-ethoxybenzoate [8] (0·1 mole) was added dropwise, and the mixture was heated under reflux in a dry atmosphere for 90 min. The product was hydrolysed and acidified. The crude *alcohol* deposited from the ethereal solution was washed with light petroleum and recrystallized from alcohol; it had m. p. 90° (Found: C, 82·4; H, 6·3. $C_{21}H_{20}O_2$ requires C, 82·9; H, 6·6%).

(o-*Ethoxyphenyl*)*diphenylmethanol*.—The compound was prepared by heating together ethereal solutions of phenylmagnesium bromide (0·22 mole) and ethyl *o*-ethoxybenzoate [7] (0·1 mole) for 3 hr., and hydrolyzing the product. The ethereal solution was washed with water and dried (Na_2SO_4). On removal of the bulk of the solvent, the *alcohol* was deposited as a yellow solid, which became colourless on recrystallizing from alcohol, and had m. p. 136—137° (Found: C, 82·7; H, 6·5. $C_{21}H_{20}O_2$ requires C, 82·9; H, 6·6%).

Basicity of Alcohols.—The basicity was determined by the method of Baeyer and Villiger.[9]

Potassium (o-*Ethoxyphenyl*)*diphenylmethoxide*.—A solution of the alcohol (3 g.) in xylene (25 ml.) was boiled with metallic potassium (0·4 g.) in dry nitrogen for 3 hr. After cooling, the unchanged metal was removed by means of a pointed rod, and the solution was reduced to one-third of its bulk by distillation in a stream of nitrogen. The crystals deposited on cooling consisted of *potassium* (o-*ethoxyphenyl*)*diphenylmethoxide* with 1 mol. of xylene of crystallization [Found: K, 8·7. $C_{21}H_{19}O_2K,C_6H_4(CH_3)_2$ requires K, 8·9%]. 27% of the solvent is retained after 1 hr. at 145°/20 mm. in a stream of nitrogen. The compound is rapidly hydrolyzed by moisture.

(o-*Ethoxyphenyl*)*diphenylmethane*.—Since the compound is obtained in very low yield by heating (*o*-ethoxyphenyl)diphenylacetic acid,[10] we employed the following methods.

(*a*) The solution obtained by refluxing the alcohol (5 g.) in acetic acid (25 ml.) with zinc dust

[5] Gattermann, Ehrhardt, and Maisch, *Ber.*, 1890, **23**, 1199.
[6] Bistrzycki and Herbst, *Ber.*, 1902, **35**, 3135.
[7] Bistrzycki and Herbst, *Ber.*, 1903, **36**, 3571.
[8] Cohen and Dudley, *J.*, 1910, **97**, 1741.
[9] Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.
[10] Liebig, *Annalen*, 1908, **380**, 216.

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(6 g.) for 2 hr. was filtered and allowed to cool. The methane deposited (3·3 g.) was repeatedly crystallized from alcohol; it had m. p. 67° (Found: C, 86·8; H, 6·9. Calc. for $C_{21}H_{20}O$: C, 87·5; H, 7·0%).

(*b*) A solution of the methanol (0·3 g.) in 98% formic acid (5 ml.) was kept at 100° until colourless. After cooling, it was poured into water, and the precipitated methane was repeatedly crystallized from alcohol. Its m. p. (66°) was unchanged by admixture with a specimen prepared by method (*a*).

Thermal Decomposition of Formates.—Measurements of the rate of evolution of carbon dioxide from solutions of triphenylmethanol (0·260 g.) and the *o*-methoxyl (0·290 g.) and the *o*-ethoxyl derivative (0·304 g.) in 98% formic acid (5 ml.) at 77° gave the annexed results.

The first two solutions were completely decolorized, but the solution of the ethoxyl derivative became brown as the characteristic colour of the cation was discharged.

Time (min.)	5	15	20	30	40	50	60	80	100
CO_2 (%)	5·3	29·9	38·6	53·5	63·1	67·5	70·6	73·2	75·3
Time (min.)	10	20	30	40	50	60	70	80	90
CO_2 (%)	43·5		60·3	74·0	82·1	88·0	93·5	97·0	98·5
Time (min.)	4	8	14	22	30	40	60	80	100
CO_2 (%)	22·4	27·6	34·2	38·6	41·7	46·5	53·1	56·9	62·2

(o-*Ethoxyphenyl*)*diphenylmethyl Chloride.*—(*a*) A solution of the alcohol (2 g.) in benzene (10 ml.) containing anhydrous calcium chloride was saturated with hydrogen chloride and kept for 12 hr. in a stoppered flask. The solution was siphoned off and concentrated to half-bulk. The deposited (*o-ethoxypheny*)*diphenylmethyl chloride* was filtered off, and recrystallized from light petroleum in a dry atmosphere. The colourless crystals had m. p. 144° (Found: Cl, 11·1. $C_{21}H_{19}OCl$ requires Cl, 10·9%).

(*b*) A suspension of the alcohol (2 g.) in light petroleum (10 ml.) was treated with acetyl chloride (2 ml.), and boiled for 45 min., then kept overnight, and the deposited (*o*-ethoxyphenyl)-diphenylmethyl chloride was recrystallized from the same solvent. It had m. p. 115° (Found: Cl, 10·7%). This procedure gave a more readily purified product than method (*a*).

The *ferric chloride addition compound* was prepared by adding an ethereal solution of anhydrous ferric chloride to a solution of (*o*-ethoxyphenyl)diphenylmethyl chloride in 1 : 1 ether–benzene. It was a greenish-black solid (Found: Cl, 28·7. $C_{21}H_{19}OCl,FeCl_3$ requires Cl, 29·2%). The *zinc chloride addition compound* was obtained similarly as a black oil which solidified in a desiccator in 3 days (Found: Cl, 24·3. $C_{21}H_{19}OCl,ZnCl_2$ requires Cl, 23·2%). The *stannic chloride addition compound* was deposited as a reddish-brown oil from benzene (Found: Cl, 31·1. $C_{21}H_{19}OCl,SnCl_4$ requires Cl, 30·4%).

Alkyl (o-*Ethoxyphenyl*)*diphenylmethyl Ethers.*—A solution of (*o*-ethoxyphenyl)diphenyl-methyl chloride (2 g.) in methanol (25 ml.) was kept at 66° in a dry atmosphere for 10 min. On concentration to half bulk and cooling, (*o-ethoxyphenyl*)*diphenylmethyl methyl ether* was deposited; recrystallized from ligroin, it had m. p. 121° (Found: C, 82·6; H, 7·0. $C_{22}H_{22}O_2$ requires C, 83·0; H, 7·0%). The chloride and ethanol gave similarly (*o-ethoxyphenyl*)*diphenyl-methyl ethyl ether*, m. p. 124° (from ligroin) (Found: C, 83·05; H, 7·0. $C_{23}H_{24}O_2$ requires C, 83·1; H, 7·3%).

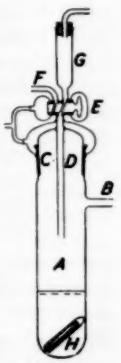
(o-*Ethoxyphenyl*)*diphenylmethyl Phenyl Ether.*—Metallic potassium (0·4 g.) was dissolved in molten phenol (7·5 g.). To the cold mass a solution of (*o*-ethoxyphenyl)diphenylmethyl chloride (1·2 g.) in ether (25 ml.) was added, and the mixture was heated on the water-bath for 30 min. The cooled mixture was extracted with ether, and the combined extracts were washed repeatedly with sodium hydroxide solution. The ethereal solution was heated to remove the solvent, and the residual (*o*-ethoxyphenyl)diphenylmethyl phenyl ether was converted into a white powder by trituration with light petroleum. After recrystallization from 1 : 1 ether–light petroleum, it had m. p. 110° (Found: C, 84·5; H, 5·7. $C_{27}H_{24}O_2$ requires C, 85·2; H, 6·4%).

The Free Radical, (o-*Ethoxyphenyl*)*diphenylmethyl.*—Absorption of oxygen by a bromo-benzene solution (10 ml.) of (*o*-ethoxyphenyl)diphenylmethyl chloride (0·462 g.) when agitated with molecular silver (6·4 g.) at 17° was slower than for triphenylmethyl chloride.

A 2% benzene solution of (*o*-ethoxyphenyl)diphenylmethyl undergoes no appreciable change in colour (Lovibond tintometer) in a sealed tube for 3 days in the dark. After longer periods, the colour is discharged; the radical is more prone than triphenylmethyl to undergo disproportionation and/or isomerization. The rapid absorption characteristic of the oxidation of the radical corresponds to 0·95 mol. of oxygen, and is practically the same as that recorded for

triphenylmethyls containing methoxyl substituents. Solutions of (*o*-ethoxyphenyl)diphenylmethyl are rapidly decolorized in sunlight owing to photochemical decomposition.

The ethane was isolated in an apparatus (Figure), which has several advantages over the Gomberg isolation unit.[11] It consists of a boiling tube *A* (13 cm. long; 2·9 cm. diam.) with a side-tube *B* and a glass stopper *C* through which passes a tube *D* sealed to a 3-way stopcock *E* in communication with a gas inlet tube *F* and a funnel *G* (6 cm. long; 1·8 cm. diam.). The vessel contains a sealed tube *H* charged with mercury and roughened on the outside to serve as "internal scratcher" for inducing crystallization. To prevent intrusion of atmospheric oxygen into the apparatus during the concentration and drying, the ground-glass joint and the stopcock are surrounded with small balloons which are kept inflated with carbon dioxide from an auxiliary generator.



A 10% solution of the radical in benzene was prepared in a Schlenk tube in the dark, and introduced under pressure of carbon dioxide into the isolation unit through the funnel *G*, which was then fitted with a stopper carrying an inlet tube in communication with the gas circuit. With the stopcock open to *F*, the lower part of the isolation unit was immersed in water at 40°, and the benzene was distilled through the side-tube under reduced pressure in a stream of carbon dioxide. On cooling of the concentrated solution, the ethane was deposited as a brown oil. Light petroleum (5 ml.) was introduced from the funnel *G*, and the oil was triturated with the solvent by oscillating the scratcher *H*. The petroleum was decanted through the side-tube *B* into a trap, and the trituration was repeated with further quantities of light petroleum until the oil was converted into a yellowish-brown powder. The ethane was deposited as yellow crystals on cooling of its solution in acetone, and was dried under reduced pressure in a stream of carbon dioxide. In an evacuated tube it had m. p. 144° (decomp.); it dissolved readily in liquid sulphur dioxide to form a red solution.

Dissociation of Di-(o-ethoxyphenyl)tetraphenylethane.—The degree of dissociation of the ethane in benzene was determined by the indirect cryoscopic method [10] with the annexed results. Each set of determinations was completed within 3 hr., during which disproportionation was negligible.

M of radical = 287·36. *M* of the ethane = 574·7.
Benzene, $K = 52·5°$.

Solvent (g.)	Chloride (g.)	Radical (g.)	Δ	*M*	Dissocn. of ethane (%)
21·98	0·4802	0·4275	0·220°	464·1	23·8
	0·6148	0·5474	0·272	480·7	19·6
17·58	0·2850	0·2337	0·157	482·6	19·1
	0·4014	0·3573	0·225	474·3	21·1
21·98	0·3682	0·3277	0·162	483·7	18·9
	0·5264	0·4686	0·236	474·3	21·1

After completion of the measurements the reddish-yellow solution was decanted from silver and silver chloride and allowed to evaporate in the air. (*o-Ethoxyphenyl)diphenylmethyl peroxide* was deposited, and after rapid recrystallization from benzene had m. p. 143—144° (Found: C, 82·9; H, 6·7. $C_{42}H_{38}O_4$ requires C, 83·1; H, 6·3%).

Absorption of Iodine by the Radical.—A solution of the chloride (0·4234 g.) in benzene (8 ml.) was reduced with molecular silver in a sealed tube with a thin-walled bulb at the bottom. The tube was broken under carbon dioxide in a sintered-glass filter-tube so that the solution passed into a flask where it was titrated with 0·1N-iodine in benzene. The weight of halogen absorbed at 15° was 0·1664 g., which is 60·3% of the amount required for complete conversion of the radical into (*o*-ethoxyphenyl)diphenylmethyl iodide.

TATEM LABORATORIES, UNIVERSITY COLLEGE, CARDIFF. [*Received, February 28th*, 1957.]

[11] Part II, *J.*, 1939, 39.

XUM

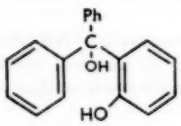
853. ***Free Radicals and Radical Stability. Part XV.* The Properties of (o-Hydroxyphenyl)diphenylmethanol and (3-Hydroxy-2-naphthyl)diphenylmethanol.***

By S. T. Bowden and K. I. Beynon.

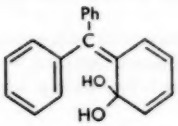
The colour developed on heating solutions of (*o*-hydroxyphenyl)- and (3-hydroxy-2-naphthyl)-diphenylmethanol is not due to the formation of the carbonium ion. The phenomenon, previously ascribed to the formation of the *o*-quinonoid isomer, is considered to be due to thermochromism. Decomposition of the alcohols at elevated temperatures is explained in terms of a free-radical mechanism which does not involve formation of quinonoid intermediates.

The hydroxyl substituent in the carbonium ion produces a bathochromic shift in the absorption spectrum, and promotes sulphonation in sulphuric acid. In the reduction of (*o*-hydroxyphenyl)diphenylmethanol in formic acid solution the total amount of carbon dioxide evolved is practically the same as with triphenylmethanol.

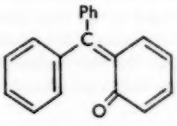
Solutions of (*o*-hydroxyphenyl)diphenylmethanol (I) in acetic acid become increasingly brown when heated from about 50° to 110°, and the changes are reversed on cooling; above 110°, however, the alcohol decomposes with elimination of water. Gomberg and Nishida [1] suggested that the development of colour is due to the quinonoid isomer (II), and that elimination of water above 110° leads to the formation of the fuchsone (III)



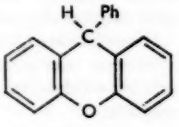
(I)



(II)

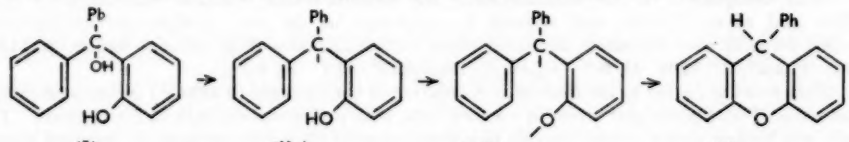


(III)



(IV)

which undergoes immediate conversion into the colourless xanthan (IV). Even if we assume that intramolecular hydrogen bonding [2] stabilizes the quinonoid isomer (II), it is not possible to account for the observed phenomena on this basis. Our preliminary studies of the absorption spectra of hot solutions of the alcohol in acetic acid show that the colour is not due to the carbonium ion and that the phenomenon is a type of thermochromism arising from the broadening of a near-ultraviolet absorption band.[3] The fact that no colour is developed on heating aniline, pyridine, or quinoline solutions is doubtless due to the formation of solvent complexes which do not exhibit thermochromism.



(I) (IIa) (IIIa) (IV)

If we accept the above hypothesis, the conversion of the alcohol into the xanthan at >110° must proceed by a mechanism which does not involve the decomposition of a quinonoid isomer. There are many indications of the thermal instability of triarylmethane derivatives: *e.g.*, triphenylmethyl iodide is *ca.* 20% dissociated in 5% benzene

* Part XIV, preceding paper.

[1] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1923, **45**, 190.

[2] Davies, *Trans. Faraday Soc.*, 1940, **63**, 333, 1114; Bergmann, "Isomerism and Isomerisation," Interscience Publ. Inc., New York, 1948, p. 18; Albrecht and Corey, *J. Amer. Chem. Soc.*, 1939, **61**, 1087.

[3] Grubbe and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419; Hirshberg and Fischer, *J.*, 1953, 629.

solution at room temperature.[4] Although triphenylmethanol is much more stable, its solution in diphenyl becomes yellow at 240° and the colour persists on cooling to the f. p. It appears, therefore, that the C–OH bond in triphenylmethanol is weaker than has been formerly supposed and that it undergoes homolytic fission at high temperatures to form triphenylmethyl and hydroxyl radicals. If the corresponding weakening of the link in (*o*-hydroxyphenyl)diphenylmethanol is such that homolytic fission sets in at 110°, formation of the xanthan may be explained according to the annexed scheme. Above 110° the hydroxyl group attached to the methane-carbon atom is released as the neutral radical while the residual triarylmethyl (IIa) undergoes redistribution of electron density and approaches the planar configuration. The electronic reorganization leads to a change in the polarity of the O–H link of the ring substituent so that it becomes susceptible to attack by the free hydroxyl with formation of water and the diradical (IIIa). Rearrangement of the latter involves the migration of a hydrogen atom from the *ortho*-position of one of the unsubstituted rings to the methyl-carbon atom to form the xanthan.

The above hypothesis may also be applied to account for the development of colour in acetic acid solutions of (3-hydroxy-2-naphthyl)diphenylmethanol at 80°. In this system, however, the change is not completely reversible, owing to the proximity of the temperature at which colour is developed to that at which decomposition of the alcohol sets in. The latter process involves formation of the corresponding diradical which is converted into the xanthan and coloured products.

The alcohols give rise to carbonium ions in sulphuric acid, and the presence of the *o*-hydroxyl group in the triphenylmethyl and 2-naphthyldiphenylmethyl ions leads to a bathochromic shift in the absorption spectrum. The ions are sulphonated in the 98% acid, and the rates of sulphonation are in the sequence: (*o*-hydroxyphenyl)diphenylmethyl > (3-hydroxy-2-naphthyl)diphenylmethyl > (3-methoxy-2-naphthyl)diphenylmethyl. On the other hand, the presence of the hydroxyl substituent increases the resistance of the triarylmethyl sulphate towards hydrolysis.

In hot formic acid solution the (*o*-hydroxyphenyl)diphenylmethyl cation is reduced to the methane, but, in contrast to the behaviour of the corresponding methoxyl derivative,[5] the favourable influence of the substituent is apparent only in the early stages of the reaction, and the total amount of carbon dioxide evolved is substantially the same as in the reduction of the triphenylmethyl ion.

Experimental

Preparation of Materials.—(*o*-Hydroxyphenyl)diphenylmethanol was prepared by hydrolyzing the product of interaction of phenylmagnesium bromide and methyl salicylate.[6] (3-Hydroxy-2-naphthyl)diphenylmethanol was obtained similarly from methyl 3-hydroxy-2-naphthoate,[7] and was converted into (3-methoxy-2-naphthyl)diphenylmethanol by means of dimethyl sulphate.[8] The alcohols and the solvents employed in the colorimetric experiments were rigorously purified by standard methods.

Action of Heat on Alcohol Solutions.—A solution of the dry alcohol was prepared in a stoppered test-tube provided with a thermometer, stirrer, and calcium chloride guard-tube. The vessel was heated in a bath of glycerol in order to determine the temperature at which the solution became coloured. The temperature at which the colour disappeared on cooling was also noted. The system was then heated to a selected temperature, and the colour of the solution was measured in Lovibond units by means of a tintometer. In Table 1 t represents in the temperature (°c) at which colour appears on heating, t' that at which the colour disappears on cooling the solution, and t'' that at which the colour measurements were made. It is evident that t depends on the nature of the solvent and that t' is generally about 5° lower than t. The solutions of (3-hydroxy-2-naphthyl)diphenylmethanol lost much of their colour on cooling,

[4] Gomberg, *J. Amer. Chem. Soc.*, 1902, **24**, 597.
[5] Part VIII, *J.*, 1940, 874.
[6] Baeyer, *Annalen*, 1907, **354**, 167.
[7] Kauffman and Egner, *Ber.*, 1913, **46**, 3782.
[8] Gomberg and McGill, *J. Amer. Chem. Soc.*, 1925, **47**, 2392.

but were not completely decolorized on attaining room temperature. Solutions of either alcohol in aniline, pyridine, or quinoline did not change colour at 120°.

The absorption spectrum of (*o*-hydroxyphenyl)diphenylmethanol in acetic acid at 57° was determined by means of a Unicam S.P. 500 spectrophotometer provided with a water-jacketed cell-holder. The absorption curve shows no maximum in the visible region, and thus differs entirely from that of the solution containing sulphuric acid which has two characteristic peaks. The colour of the former solution, therefore, is not due to the carbonium ion.

TABLE 1. *Colour of alcohol solutions.*

	(*o*-Hydroxyphenyl)diphenylmethanol (5%)					(3-Hydroxy-2-naphthyl)-diphenylmethanol (2·5%)			
				Lovibond units				Lovibond units	
Solvent	*t*	*t'*	*t''*	red	yellow	*t*	*t''*	red	yellow
Acetic acid	55	50	100	8·9	9·0	80	100	0	3·3
Me benzoate	110	100	120	0·1	0·1	150	150	3·0	7·0
n-Pentyl ether	85	80	85	1·0	2·0	—	—	—	—
Benzophenone	90	85	95	2·3	5·0	90	130	0	1·3
Benzene	55	55	80	3·0	4·5	70	80	0	0·4
o-Xylene	—	—	—	—	—	120	135	0	0·6
Diphenyl	64	—	100	13·5	9·0	85	100	0	1·1
Naphthalene	60	50	100	15·0	9·9	100	115	0·5	3·0

Action of Sodium on (o-*Hydroxyphenyl*)*diphenylmethanol.*—A solution of the alcohol (0·276 g.) in boiling xylene (75 ml.) was treated with metallic sodium (0·50 g.) in a vessel attached to a gas-burette for measuring the volume of hydrogen evolved. The gas evolved in 40 min. corresponded to the replacement of the hydrogen atoms of both hydroxyl groups. The suspension of the *disodium derivative* was removed from unchanged metal and kept in a dry atmosphere. The deposited crystals were filtered off, washed with xylene and light petroleum, and dried over silica gel and paraffin wax in a vacuum-desiccator (Found: Na, 13·7. $C_{19}H_{14}O_2Na_2$ requires Na, 14·4%).

Absorption Spectra of Carbonium Ions.—The absorption spectra of sulphuric acid solutions of the alcohols were determined at room temperature, and the main features are indicated in Table 2. The absorption curve of (*o*-hydroxyphenyl)diphenylmethanol in acetic acid containing 1% sulphuric acid differed from that of the compound in 98% sulphuric acid, and in the latter solution sulphonation was complete before measurements could be undertaken. The stabilities of the ions in 80% sulphuric acid were found to conform to the sequence: (3-methoxy-2-naphthyl)diphenylmethyl > (3-hydroxy-2-naphthyl)diphenylmethyl > (*o*-hydroxyphenyl)diphenylmethyl.

TABLE 2. *Absorption spectra of carbonium ions.*

Carbonium ion	Concn. of acid (%)	$\lambda_{max.}$ (mμ)	$10^{-4} \times \varepsilon_{max.}$	Remarks
(*o*-Hydroxyphenyl)diphenyl-	98	370, 440	3·20	No change in 24 hr.
(3-Hydroxy-2-naphthyl)diphenyl	98	440, 480	4·63	Rapid change
	80	426, 490	—	No change in 24 hr.
(3-Methoxy-2-naphthyl)diphenyl	98	432, 473	4·81	Slight change in 1 week

Basicity of Alcohols.—The basicity of the hypothetical base as measured by the stability of the triarylmethyl sulphate towards hydrolysis was determined by a modification of the method of Baeyer and Villiger [9] of two solutions of the alcohol (0·0003 mole) in acetic acid (5·0 ml.); one served as a control while the other was treated with a 10% solution of sulphuric acid in acetic acid (5 ml.) to convert the alcohol into the coloured sulphate. The latter was titrated with a 75% aqueous solution of ethyl alcohol, and the colour change was followed by means of a photoelectric colorimeter, whose scale had been previously adjusted to zero by means of the control solution. Addition of the aqueous solution was continued until the optical density of the carbinol solution attained a constant value which was generally zero. The basicity of triphenylmethanol being taken as unity, the results were: (*o*-hydroxyphenyl)-, 2·4; (3-hydroxy-2-naphthyl)-, 3·9; (3-methoxy-2-naphthyl)-, 1·3.

[9] Baeyer and Villiger, *Ber.*, 1902, **35**, 489.

Reduction of Alcohols in Formic Acid.—The rate of evolution of carbon dioxide from a solution of the alcohol (0·001 mole) in 98% formic acid (10 ml.) at 76·5° was measured in the apparatus previously described.[8] The behaviour of triphenylmethanol was examined under similar conditions with the tabulated results.

Triphenylmethanol.

Time (min.)	3	8	13	18	23	33	43	53	73
CO_2 (%)	6·15	29·1	43·7	50·7	54·3	58·2	60·9	62·6	64·7

(o-*Hydroxyphenyl*)*diphenylmethanol.*

Time (min.)	5	10	15	20	25	30	40	50	70
CO_2 (%)	22·1	39·9	45·4	48·7	52·2	54·4	58·2	60·0	61·8

The favourable influence of the hydroxyl group is evident in the early stages of the reaction but this effect is not sustained as in the case of the methoxyl group in the *o*-position.[5] The solution of the (*o*-hydroxyphenyl)diphenylmethyl derivative deposited the methane, m. p. and mixed m. p. 124° (from alcohol), on treatment with water.

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[*Received, February, 28th,* 1957].

[10] Baeyer, *Annalen*, 1907, **354**, 178.

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854. *Free Radicals and Radical Stability. Part XVI.* The Properties of Triarylmethanols containing* p-*Hydroxyl Substituents, and the Quinonoidation Theory of Free Radicals.*

By K. I. BEYNON and S. T. BOWDEN.

Diphenylquinomethane and the so-called colourless and coloured forms of (*p*-hydroxyphenyl)diphenylmethanol give the same carbonium ion in sulphuric acid, and their hot formic acid solutions evolve carbon dioxide at practically the same rate.

Although American investigators maintain that the product obtained on crystallizing the alcohol from acetic acid is a quinonoid isomer, the present analysis of the absorption spectra of mixtures of colourless alcohol and diphenylquinomethane and the *X*-ray and thaw-melt examination of the solid systems indicate that the colour is due to the presence of the fuchsone. The properties of other triarylmethanols containing *p*-hydroxyl substituents may be accounted for on a similar basis.

If, as indicated, quinonoid forms of these compounds have no independent existence, Gomberg's main evidence in support of the quinonoidation theory of free radicals is no longer valid.

(*p*-HYDROXYPHENYL)DIPHENYLMETHANOL is peculiar in that when deposited from solution in ammoniacal alcohol the crystals are colourless and melt with decomposition at 159—160°, whereas when obtained from 50% acetic acid they are yellow and melt with decomposition at 138—139°. The two products are not polymorphs, and Gomberg *et al.*,[1] and more recently Anderson *et al.*,[2] maintain that the colourless product is the benzenoid alcohol (I) and that the coloured product has the quinonoid structure (II). On the contrary, Ramart-Lucas and Martynoff [3] contend that the coloured product is simply a mixture of the benzenoid alcohol (I) and diphenylquinomethane (III), but their meagre evidence is not entirely convincing.

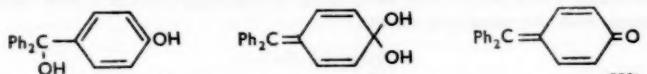
* Part XV, preceding paper.

[1] Gomberg, *J. Amer. Chem. Soc.*, 1913, **35**, 1035; Gomberg and Van Stone, *ibid.*, 1916, **38**, 1577; Gomberg and Sullivan, *ibid.*, 1920, **42**, 1864; Gomberg and Lange, *ibid.*, p. 1874; Gomberg and Anderson, *ibid.*, 1928, **50**, 203.

[2] Anderson, *ibid.*, 1929, **51**, 1889; Anderson and Geiger, *ibid.*, 1932, **54**, 3059; Anderson and Fisher, *ibid.*, 1944, **66**, 594.

[3] Ramart-Lucas and Martynoff, *Bull. Soc. chim. France*, 1941, **8**, 882.

The investigations have been largely concerned with the absorption spectra of the substances in ethereal solution and, while the absorption curves determined in the present



(I) (II) (III)

work are similar to those obtained by previous investigators, it is evident from the following data that the values of $\varepsilon_{max.}$ estimated from the curves given by Ramart-Lucas and Martynoff are substantially lower than those found by us.

Absorption spectra of ethereal solutions.

	$10^{-3}\varepsilon_{max.}$			Absorption max. (mμ)		
	Anderson and Gomberg	Ramart-Lucas and Martynoff	Present work	Anderson and Gomberg	Ramart-Lucas and Martynoff	Present work
Colourless product.....	2·2	1·0	2·14	278, 285	278, 285	278, 285
Coloured product	2·2	1·5	2·16	278, 285, 365	278, 285, 365	278, 285, 365
Diphenylquinomethane	30·2	21·4	27·6	260, 365	260, 365	260, 365

If the peak at 365 mμ is due solely to diphenylquinomethane, the concentration of the latter may vary from 0·67 to 0·88%. Our absorption curves for mixtures of colourless (*p*-hydroxyphenyl)diphenylmethanol and the fuchsone are shown in the Figure. The observed values of the optical densities agree closely with those calculated on the basis of Beer's law, and the curve for the mixture containing 99·22% of the colourless alcohol and 0·78% of the fuchsone is indistinguishable from that of the coloured product. We conclude that the coloured product is a mixture and that its composition varies slightly according to the conditions of crystallization.

The alcohol and the coloured product give the same *X*-ray diffraction patterns, the method not revealing less than 5% of diphenylquinomethane. Thermal analysis of mixtures prepared by grinding together the colourless alcohol and diphenylquinomethane indicates that the components form a 1 : 1 compound, but it is not possible to determine the solid solubility at low fuchsone concentrations owing to the thermal instability of the alcohol.

The most striking difference between the alcohol and the coloured product is the more rapid elimination of water from the latter at about 90°. This arises only in the solid state where specific factors governing the formation and growth of nuclei of the solid decomposition product determine the rate of the reaction. If the reaction involves the formation of diphenylquinomethane hydrate as intermediate phase, decomposition of the latter will be induced by nuclei of fuchsone, which are already present in the coloured product. The different thermal behaviour of mixtures of colourless alcohol and diphenylquinomethane prepared by mechanical grinding and the product precipitated from alcoholic solution by water may be explained similarly.

The hydroxyl group exerts an overall inhibitory effect on the reduction of the alcohol in hot formic acid, and since solutions of the colourless alcohol, coloured product, and fuchsone evolve carbon dioxide at practically the same rate, the reactions may be represented:

$$HO{\cdot}C_6H_4{\cdot}CPh_2{\cdot}OH + H{\cdot}CO_2H \rightleftharpoons HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^- + H_2O$$

$$O{:}C_6H_4{:}CPh_2 + H{\cdot}CO_2H \rightleftharpoons HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^-$$

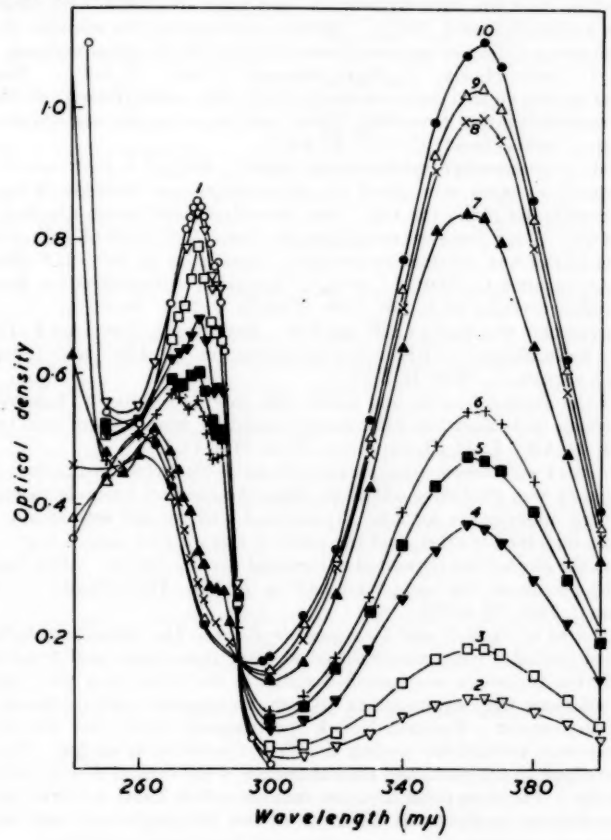
$$HO{\cdot}C_6H_4{\cdot}C^+Ph_2 + H{\cdot}CO_2^- = HO{\cdot}C_6H_4{\cdot}CHPh_2 + CO_2$$

There is, moreover, no appreciable difference between the basicities of the colourless alcohol and the coloured product as measured by the salt-hydrolysis method.

The coloured products obtained by crystallizing (4-hydroxy-3 : 5-dimethoxyphenyl)-diphenylmethanol and diphenyl-(3 : 4 : 5-trihydroxyphenyl)methanol from 50% acetic

acid are mixtures of the alcohol and fuchsone. On the other hand, *X*-ray and chemical analysis reveals that the yellow products obtained by similar treatment of (2 : 4-dihydroxyphenyl)- and (4-hydroxy-2-methylphenyl)-diphenylmethanol are complexes containing acetic acid of crystallization. The properties of the alcohols examined in the present work may thus be explained without recourse to the quinonoidation theory.

Absorption spectra of (p-*hydroxyphenyl*)*diphenylmethanol and mixtures with diphenylquinomethane. Molar % of diphenylquinomethane:* (1) 0; (2) 0·78; (3) 1·56; (4) 4·22; (5) 6·05; (6) 7·33; (7) 28·4; (8) 49·7; (9) 70·4; (10) 100.



Experimental

(p-*Hydroxyphenyl*)*diphenylmethanol.*—The compound was prepared from diphenylmethylene dichloride and phenol.[4] Addition of water to a solution of the alcohol in alcohol containing a drop of 2N-ammonia gave colourless or pale yellow crystals, m. p. 159—160° (decomp.). Similar treatment of the solution in 50% acetic acid led to the separation of yellow crystals, m. p. 137—139° (decomp.).

Thermal decomposition of the alcohol gave diphenylquinomethane, m. p. 168°.[5]

(4-*Hydroxy*-2-*methylphenyl*)*diphenylmethanol.*—Prepared from diphenylmethylene dichloride and *m*-cresol,[6] this alcohol was obtained as colourless crystals, m. p. 114°. The solution in

[4] Gomberg and Jickling, *J. Amer. Chem. Soc.*, 1915, **37**, 2575.
[5] Baeyer and Villiger, *Ber.*, 1903, **36**, 216.
[6] Gomberg and Johnson, *J. Amer. Chem. Soc.*, 1917, **39**, 1674.

acetic acid on treatment with water deposited yellow crystals of the alcohol–acid complex, m. p. 80—82° (Found: C, 74·5; H, 6·4. Calc. for $C_{20}H_{16}O_3,CH_3{\cdot}CO_2H$: C, 75·4; H, 6·3%).

(2 : 4-*Dihydroxyphenyl*)*diphenylmethanol*.—Hydrolysis of the product from 2 : 4-dihydroxybenzophenone and phenylmagnesium bromide gave the alcohol, m. p. 123°. On addition of water to the solution in 50% acetic acid, the alcohol–acid complex was deposited as yellow crystals, m. p. 115° (Found: C, 72·8; H, 5·6. $C_{19}H_{16}O_3,CH_3{\cdot}CO_2H$ requires C, 71·6; H, 5·7%).

Diphenyl-(3 : 4 : 5-*trihydroxyphenyl*)*methanol*.—A solution of methyl gallate (1 equiv.) in ether was added to phenylmagnesium bromide (4 equiv.), and the mixture was heated and shaken under reflux for 4 hr., then hydrolysed, and after treatment with steam the alcohol was obtained as a dark red solid (18%). Addition of water to the solution of the *alcohol* in 50% alcohol containing a drop of aqueous ammonia gave small yellow crystals, m. p. 183·5—184·5° (Found: C, 74·9; H, 4·9. $C_{19}H_{16}O_4$ requires C, 74·0; H, 5·2%). Recrystallization from ammoniacal alcohol yielded dark red needles, m. p. 183—184° (Found: C, 76·8; H, 4·7%). After repeated recrystallization from 50% acetic acid the material was obtained as reddish-brown crystals, m. p. 167° (Found: C, 75·7; H, 5·2%).

(4-*Hydroxy*-3 : 5-*dimethoxyphenyl*)*diphenylmethanol*.—Methyl 4-hydroxy-3 : 5-dimethoxybenzoate [7] (1 equiv.) in ether was added to phenylmagnesium bromide (4 equiv.), and the mixture was heated under reflux for 4 hr., then hydrolyzed and steam-distilled, giving a pale yellow solid (83%). After three recrystallizations from 50% alcohol containing a drop of 2N-ammonia, the *alcohol* was obtained as colourless crystals, m. p. 210—212° (Found: C, 74·9; H, 5·9. $C_{21}H_{20}O_4$ requires C, 75·0; H, 6·0%). Repeated recrystallization from 50% acetic acid gave deep yellow crystals, m. p. 198—199° (Found: C, 74·4; H, 6·1%).

The colourless alcohol was kept at 150° for 4 hr. Recrystallisation from 1 : 1 ether–benzene gave yellow (3 : 5-*dimethoxyphenyl*)*phenylquinomethane*, m. p. 225—226° (Found: C, 77·2; H, 5·7. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%).

Reduction of the alcohol by zinc and acetic acid gave (4-*hydroxy*-3 : 5-*dimethoxyphenyl*)*diphenylmethane* which was colourless after recrystallization from alcohol and had m. p. 131° (Found: C, 78·0; H, 5·9. $C_{21}H_{20}O_3$ requires C, 78·8; H, 6·1%).

(3 : 5-*Dihydroxy*-4-*methoxyphenyl*)*diphenylmethanol*.—Methyl 3 : 5-dihydroxy-4-methoxybenzoate [8] (1 equiv.) was gradually added to phenylmagnesium bromide (4 equiv.), and the mixture was heated under reflux for 3 hr., hydrolyzed, and treated with steam. The residual dark red solid was dissolved in ether, and the solution was warmed with " Norit " and filtered. On concentration the *alcohol* was deposited as dark red needles (35%). After three recrystallizations from light petroleum the compound had m. p. 174—175° (Found: C, 75·6; H, 5·3. $C_{20}H_{18}O_4$ requires C, 74·5; H, 5·6%).

Absorption Spectra of Alcohols and Fuchsones in Ether.—The colourless alcohols and corresponding coloured products were recrystallized at least three times and dried over soda-lime before use, while the fuchsones were purified similarly and dried over silica gel and calcium chloride. The solutions were examined in 10 mm. rectangular cells by means of a Unicam S.P. 500 spectrophotometer. Eastman-Kodak Spectro-grade ethyl ether was the solvent, and evaporation losses were reduced by binding the lid of the cell with tin foil. As far as possible the solutions were kept in the dark, and measurements of the optical density were made in the range 225—500 mμ. The absorption data are summarized in Table 1, where the first value of the maximum extinction coefficient is the mean of two determinations, and the other values refer to solutions prepared from different specimens of the alcohol or fuchsone.

Although the absorption spectra of the so-called colourless and coloured forms of (*p*-hydroxyphenyl)diphenylmethanol are similar in the ultraviolet region, the coloured product exhibits a low absorption peak at a wavelength corresponding to the maximum absorption of the fuchsone. On the basis of Beer's law it may be shown that a mixture containing 99·48% of the colourless carbinol and 0·52% of the fuchsone gives essentially the same absorption band as the coloured product and that the optical density in the ultraviolet region (278 mμ) differs by only 0·8% from that of the colourless alcohol.

A mixture containing 99·48% of colourless alcohol and 0·58% of fuchsone, prepared by grinding the components, melted at 137—158° whereas the " coloured alcohol " had m. p. 137—139°. On the other hand, the yellow crystals obtained by adding water to an alcoholic

[7] Robinson and Bradley, *J.*, 1928, 1555.
[8] Graebe and Martz, *Ber.*, 1903, **36**, 216.

solution containing the components in the above proportions melted at 136·5—139°, and the m. p. was unchanged on admixture with the " coloured alcohol."

The absorption spectra of various mixtures of (*p*-hydroxyphenyl)diphenylmethanol (m. p. 160·0°) and diphenylquinomethane in ether are shown in the Figure. For each mixture there is very good agreement between the observed values of the optical densities at various wavelengths and those calculated on Beer's law. The curve of a mixture containing 99·22% of

TABLE 1. *Absorption spectra of alcohols, coloured products, and fuchsones in ether.*

Diphenylmethanol	Coloured product	$10^{-4}\varepsilon_{max.}$	$\lambda_{max.}$ (mμ)
(*p*-Hydroxyphenyl)-	—	0·216	278, 285
	Yellow	0·221	278, 285, 365
(4-Hydroxy-2-methylphenyl)-	—	0·157	278, 284
	Yellow	0·152	278, 284
(3 : 4 : 5-Trihydroxyphenyl)-	Yellow	1·29	267, 393
	Red	1·31	267, 395
	Brown	1·27	267, 393
(4-Hydroxy-3 : 5-dimethoxyphenyl)-	—	0·162	*268, *285
	Yellow	0·169	*268, *285, 378
Quinomethane			
Diphenyl		2·79	261, 365
(3 : 5-Dimethoxyphenyl)phenyl		2·61	265, 378

* Inflexion.

colourless alcohol and 0·78% of diphenylquinomethane is indistinguishable from that of the coloured product.

X-*Ray Diffraction Measurements.*—Preliminary experiments showed that the extent of conversion of colourless alcohol into coloured product during the measurements is small.

(a) *Powder photographs.* The diffraction patterns of the two specimens are identical with respect to the position and relative intensity of the bands. Similar remarks apply to (4-hydroxy-3 : 5-dimethoxyphenyl)diphenylmethanol. With diphenyl-(3 : 4 : 5-trihydroxyphenyl)-methanol, however, the diffraction pattern of the red product is different from those of the yellow and brown products, which are practically identical.

(b) *Single-crystal method.* Single crystals of the colourless and coloured products were examined by means of the Unicam single crystal goniometer (Stubbins), with Cu-K_α radiation for 1 hr. The unit cells were identical: $a = 8{\cdot}6$, $b = 10{\cdot}6$, $c = 15{\cdot}4$ Å, $\beta = 100°$.

Thermal Analysis of Mixtures.—A preliminary study was made with mixtures of triphenylmethanol and diphenylquinomethane. In the first method, weighed amounts of the two components were intimately mixed by fusion before thermal analysis, but in the second method the mixtures were prepared by mechanical grinding. The thaw points and melt points of mixtures prepared by the two methods are in Table 2. The data obtained by method 1 show

TABLE 2. *Triphenylmethanol and diphenylquinomethane.*

Method 1

Diphenylquinomethane (molar %)	0	9·6	23·7	38·4	40·0	50·0	53·3	57·5	62·5	75·9	78·4	100
Thaw point	162°	120°	120°	120°	120°	126°	115°	115°	116°	115°	115°	168°
Melt point	162°	151°	130°	123°	123°	126°	125°	121°	122°	149°	152°	168°

Method 2

Diphenylquinomethane (molar %)	0	10·0	25·0	35·0	50·0	55·0	70·0	90·0	100
Thaw point	162°	121°	121°	121°	124°	116°	116°	116°	168°
Melt point	162°	144°	126°	122°	125°	125°	144°	158°	168°

that the components form a 1 : 1 compound with congruent m. p. 126°, and that the two eutectic mixtures containing 30·5% and 60·5% of the fuchsone melt at 120° and 115°, respectively. Although the thaw points and melt points of mixtures prepared by method 2 may differ by several degrees from those found for mixtures prepared by method 1, the data indicate the main features of the solid–liquid equilibria.

The system (*p*-hydroxyphenyl)diphenylmethanol and diphenylquinomethane can be investigated by method 2 only as the alcohol decomposes in the solid state to form the fuchsone and water. The temperatures corresponding to thaw points and melt points accordingly depend

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on the rate of heating, and in the present experiments the tubes containing the mixture were rapidly heated by immersion in a bath at 120°, and the temperature then raised at a rate of 0·3° per min. Table 3 shows that the two components form a 1 : 1 compound (m. p. 146°) and

TABLE 3. *(p-Hydroxyphenyl)diphenylmethanol and diphenylquinomethane.*

Diphenylquinomethane (molar %)	0	5·0	10·0	25·0	30·0	40·0	50·0	60·0	75·0	90·0	100
Thaw point	161°	137°	137°	138°	136°	137°	138°	138°	139°	138°	168°
Melt point	161°	154°	148°	142°	139°	145°	146°	142°	145°	160°	168°

that the two eutectic mixtures containing 27·5% and 65·0% of diphenylquinomethane melt at 137° and 138°, respectively. The compound had been prepared previously by maintaining (*p*-hydroxyphenyl)diphenylmethanol at 90°, and its m. p. is reported to be 150° by Baeyer and Villiger [5] and 144° by Ramart-Lucas and Martynoff.[3] Owing to thermal instability of the alcohol the present method could not be applied to determine the limits of solid solubility in the system. It is possible, however, that a solid solution of diphenylquinomethane in the alcohol is produced when a solution of the components in ethanol at ordinary temperatures is treated with water.

Rate of Elimination of Water.—The rate of elimination of water in boiling organic liquids was measured in an entrainment-distillation apparatus. (*p*-Hydroxyphenyl)diphenylmethanol and the coloured product are completely soluble in boiling *iso*propyl ether (b. p. 69°), and the two solutions lost water at practically the same rate. On the other hand, the colourless alcohol and the coloured product are insoluble in *n*-hexane, and with this liquid the rate of elimination of water from the coloured product was almost double that from the colourless one, in harmony with Gomberg's observations [1] of a similar difference in the decomposition rates at 90°.

Action of Sodium.—Solutions of (*p*-hydroxyphenyl)diphenylmethanol and the coloured product in boiling xylene were treated with metallic sodium, and the volume of hydrogen evolved was measured at intervals. The gas was evolved at practically the same rate from the two systems and the total volume corresponded to the formation of the disodium derivative. During the experiments there was partial decomposition of the alcohol into water and diphenylquinomethane, and the solution became coloured owing to interaction of the latter with the metal. The insoluble disodium derivative obtained as a white powder after washing of the precipitated mass with anhydrous xylene was difficult to free from the adherent liquid (Found: Na, 12·8, 13·5. Calc. for $C_{19}H_{14}O_2Na_2$: Na, 14·4%).

Absorption Spectra of Carbonium Ions.—The alcohols were recrystallized at least three times and kept in a desiccator with soda-lime and paraffin wax for 48 hr. before use. The compounds were dissolved in 98% sulphuric acid (" AnalaR ") so that the concentration of the solution was 10^{-5} mole/l. In order to ascertain whether the compounds are sulphonated under these conditions, the absorption spectrum was determined within 15 min., and again after 24 hr. in the dark. The main features of the absorption spectra are summarized in Table 4 together with the basicity values determined by the modified Baeyer method (Part XV). It is evident that *p*-substitution of hydroxyl in triphenylmethyl leads to a bathochromic shift in the absorption of the ion, and contributes strongly to the stability of the sulphate towards hydrolysis.

TABLE 4. *Absorption characteristics of sulphuric acid solutions.*

Substance		$\varepsilon_{max.} \times 10^{-4}$	$\lambda_{max.}$ (mμ)	Basicity
Diphenylquinomethane		4·20	401, 464	—
(2 : 4-Dihydroxyphenyl)phenylquinomethane		—	370, 477	—
Triphenylmethanol		3·84	408, 431	1·0
(4-Hydroxy-2-methylphenyl)diphenylmethanol		3·43	432, 473	—
(3 : 5-Dihydroxy-4-methoxyphenyl)diphenylmethanol		3·11	405, 489	21·2
(4-Hydroxy-3 : 5-dimethoxyphenyl)diphenylmethanol		3·24	400, 505	4·5
(*p*-Hydroxyphenyl)diphenylmethanol:	colourless	4·30	401, 464	30·4
	yellow	4·25	401, 464	30·7
(3 : 4 : 5-Trihydroxyphenyl)diphenylmethanol:	red	3·26	398, 498	16·3
	yellow	3·64	398, 498	—
	brown	3·04	398, 498	—

Reduction in Formic Acid.—The reduction of (*p*-hydroxyphenyl)diphenylmethanol and diphenylquinomethane in formic acid was examined by measuring the rate of evolution of gas.[6]

[6] Part VIII, *J.*, 1940, 874.

The results in Table 5 refer to the reduction of 0·001 mole of the compound in 98% formic acid (10 ml.) at 76·5°. When carbon dioxide was no longer evolved from the solution of (*p*-hydroxyphenyl)diphenylmethanol, the system was cooled and treated with water. The deposited

TABLE 5. *Reduction in formic acid.*

Triphenylmethanol									
Time (min.).....	3	8	13	18	23	33	43	53	73
CO_2 (%)	6·2	29·1	43·7	50·7	54·3	58·2	60·9	62·6	64·7
(*p*-Hydroxyphenyl)diphenylmethanol									
Colourless product									
Time (min.).....	5	10	20	25	30	40	60	80	110
CO_2 (%)	3·2	8·3	18·9	24·0	29·0	38·6	51·7	61·6	68·1
Coloured product									
Time (min.).....	5	10	15	20	30	40	60	80	110
CO_2 (%)	2·8	7·5	12·9	18·9	28·7	37·6	51·1	61·1	68·5
Diphenylquinomethane									
Time (min.).....	10	15	20	25	30	40	60	80	100
CO_2 (%)	4·7	10·5	15·9	21·9	27·9	36·1	51·0	59·8	65·6

methane was recrystallized from alcohol, and did not depress the m. p. of a specimen prepared by means of zinc and acetic acid.

We are indebted to Professor A. G. Evans for providing facilities, and to Professor A. J. C. Wilson and Dr. D. Rogers for their help with the *X*-ray measurements.

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855. *Free Radicals and Radical Stability. Part XVII.** (m-*Hydroxyphenyl)diphenylmethanol and the Corresponding Free Radical.*

By S. T. BOWDEN and K. I. BEYNON.

(*m*-Hydroxyphenyl)diphenylmethanol does not exhibit thermochromism or form a fuchsone. The carbonium ion is less readily sulphonated than the *ortho*-substituted ion.

(*m*-Hydroxyphenyl)diphenylmethyl chloride, which is stable at room temperature, is reduced by silver to the bright yellow free radical, and the corresponding ethane is the first derivative of this type to be isolated in the solid state.

Although the presence of the hydroxyl group in the radical may lead to the formation of hydrogen-bonded complexes, the observed unimolecular stability is greater than that of (*m*-methoxyphenyl)diphenylmethyl owing to the stronger inductive effect of the substituent.

(*m*-HYDROXYPHENYL)DIPHENYLMETHANOL, which is obtained colourless by recrystallization from alcohol or aqueous acetic acid, is thermally much more stable than the corresponding *ortho*- and *para*-substituted compounds (Parts XV, XVI), and its solutions may be heated to 150° without the development of colour.

The influence of the hydroxyl and methoxyl substituents on the basicity of the alcohol is shown in the annexed Table, where the values are referred to triphenylmethanol as unity. Hydroxyl raises the basicity more than does the methoxyl group,[1] and the effect is most marked with *para*-substitution. The (hydroxyphenyl)diphenylmethanols with excess of metallic sodium in xylene form the disodium derivative $(NaO{\cdot}C_6H_4)CPh_2{\cdot}ONa$,

* Parts XIII—XVI, preceding papers.

[1] Part VIII, *J.*, 1940, 874.

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and the overall reactivity, measured by the rate of evolution of hydrogen, is in the order: $p > m \gg o$.

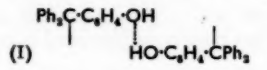
Basicity and halochromism.

Diphenylmethanol	Basicity	Sulphate	Diphenylmethanol	Basicity	Sulphate
(*o*-Hydroxyphenyl)-	2·4	Yellow	(*o*-Methoxyphenyl)-	2·0	Red
(*m*-Hydroxyphenyl)- ...	2·5	Red	(*m*-Methoxyphenyl)-	1·2	Orange-red
(*p*-Hydroxyphenyl)-	30·4	Orange	(*p*-Methoxyphenyl)-	5·6	Red

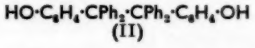
Formic acid solutions of the (hydroxyphenyl)diphenylmethanols decompose when heated, with evolution of carbon dioxide and formation of the corresponding methane.[2] The relative rates of reduction at 77° conform to the sequence: unsubstituted $\simeq o > p > m$. In the early stages of the reaction the *m*-hydroxyl substituent exerts a more favourable influence on the rate of reduction than the *p*-hydroxyl group, but this influence is soon outweighed by an inhibiting effect which leads to a low yield of the triarylmethane. This appears to be a general feature of the behaviour of *m*-substituted triarylmethyl cations, and it is also observed when the substituent is methoxyl or methyl.[1]

(*p*-Hydroxyphenyl)diphenylmethyl chloride cannot be obtained pure because it forms the fuchsone spontaneously, with elimination of hydrogen chloride, and the *ortho*-substituted compound, although obtainable pure, rapidly becomes brown as a result of similar changes.[3] On the other hand, the beautifully crystalline (*m*-hydroxyphenyl)diphenylmethyl chloride is considerably more stable and remains colourless for several weeks in a dry atmosphere. It has the characteristic properties of a triarylmethyl halide, and forms highly coloured addition complexes with ferric chloride and zinc chloride.

Gomberg and Nishida,[3] and Gomberg and Jickling,[4] could not prepare stable solutions of the free radicals (*o*-hydroxyphenyl)diphenylmethyl and (*p*-hydroxyphenyl)diphenylmethyl, but we experienced no difficulty in preparing pure (*m*-hydroxyphenyl)diphenylmethyl by reduction of the chloride in benzene solution with molecular silver. At room temperature in the absence of sunlight the free radical shows little tendency to disproportionate or isomerize, and can be examined by the customary methods. Apart from exhibiting the normal equilibrium between the hexa-arylethane and the free radical, this system presents the unusual feature that the presence of hydroxyl substituents may lead



(I)



(II)

to hydrogen bonding and the formation of complexes such as (I). If this complex functions as an independent entity in solution, its differentiation from the true ethane (II) is not possible by cryoscopy. On the other hand, hydrogen bonding between two or more molecules of the ethane (II) would increase the observed molecular weight. In view of the size of the aromatic groups, however, the concentration of such complexes is probably low and for our present purposes we assume that the observed molecular weight refers solely to the equilibrium between the ethane (II) and the free radical. The radical stability computed on this basis for the system in freezing 2% benzene solution is about 33%, which is roughly twice that found for (*m*-methoxyphenyl)diphenylmethyl (Part XIII). The strong inductive effect of the hydroxyl group stabilises the electron septet in this radical, and doubtless contributes also to the high stability of (3-hydroxy-2-naphthyl)diphenylmethyl.[5]

The free radical (*m*-hydroxyphenyl)diphenylmethyl is bright yellow in solution, and there is little loss of colour in the dark in 3 days. In sunlight, however, the solution is rapidly decolorized owing to photodecomposition of the type previously observed with

[2] Kauffmann and Panwitz, *Ber.*, 1912, **45**, 766.
[3] Gomberg and Nishida, *J. Amer. Chem. Soc.*, 1923, **45**, 190.
[4] Gomberg and Jickling, *ibid.*, 1915, **35**, 2575.
[5] Gomberg and McGill, *ibid.*, 1925, **47**, 2392.

triphenylmethyl.[6] The radical rapidly absorbs oxygen, and a crystalline peroxide has been isolated.

Although Gomberg and McGill [5] failed to isolate the ethane corresponding to (3-hydroxy-2-naphthyl)diphenylmethyl, we obtained di-*m*-hydroxyphenyltetraphenylethane as pale yellow crystals.

Experimental

(m-*Hydroxyphenyl*)*diphenylmethanol*.—The compound was prepared from phenylmagnesium bromide and methyl *m*-hydroxybenzoate.[7] On treatment of the benzene solution with light petroleum, the alcohol was deposited as colourless crystals, m. p. 148°. In contrast to the behaviour of (*o*-hydroxyphenyl)diphenylmethanol (Part XV), solutions in toluene, diphenyl, naphthalene, or acetic acid do not become coloured at 120°. Unlike (*p*-hydroxyphenyl)diphenylmethanol (Part XVI) the compound is colourless on recrystallization from 50% acetic acid. The basicity (Part XV) of (*m*-hydroxyphenyl)diphenylmethanol is 2·5.

(m-*Hydroxyphenyl*)*diphenylmethyl Chloride*.—(*a*) A few lumps of calcium chloride were added to a solution of the alcohol (2 g.) in ether (20 ml.) and the mixture was saturated at 0° with hydrogen chloride. After 24 hr. the solution was siphoned off and concentrated to half-bulk (guard-tube). The deposited (m-*hydroxyphenyl*)*diphenylmethyl chloride* (30%) was recrystallized from light petroleum in a dry atmosphere, and had m. p. 95—96° (Found: Cl, 12·2. $C_{19}H_{15}OCl$ requires Cl, 12·1%).

(*b*) A solution of the alcohol (2 g.) in acetyl chloride (6 ml.) was heated under reflux in a dry atmosphere for 30 min. (*m*-Hydroxyphenyl)diphenylmethyl chloride (70%) was deposited on allowing the solution to stand in a desiccator.

(m-*Hydroxyphenyl*)*diphenylmethyl Peroxide*.—A saturated solution (4 ml.) of (*m*-hydroxyphenyl)diphenylmethyl chloride was shaken for 20 min. with molecular silver (2 g.) in the absence of oxygen and light. The solution was decanted from silver and silver chloride and allowed to evaporate in the air. The yellow residue was triturated with light petroleum, and the solid was washed with acetone to remove coloured products. The colourless peroxide, m. p. 159°, on analysis gave a low value for C, but could not be purified further by crystallization.

Absorption Spectrum of the Alcohol in Sulphuric Acid.—Absorption spectra were determined by means of a Unicam S.P. 500 spectrophotometer. A $1·46 \times 10^{-5}$M-solution in 98% sulphuric acid had $\lambda_{max.}$ 405 and 435 mμ (ε 40,300); the spectrum changes with time. In 10 days the peak at 405 mμ degenerates to a shoulder; the peak at 435 mμ is displaced to 442 mμ and there is a 13% decrease in $\varepsilon_{max.}$. A $1·05 \times 10^{-5}$M-solution in 80% sulphuric acid had $\lambda_{max.}$ 420 mμ (ε 42,200) and was unchanged for 24 hr.

Thermal Stability of Formic Acid Solutions.—Reduction of the alcohol (0·001 mole) in 98% formic acid (10 ml.) was examined at 76·5° by measuring the rate of evolution of carbon dioxide from the solution: [1]

Triphenylmethanol

Time (min.)	3	8	13	18	23	33	43	63	73
CO_2 (%)	6·15	29·1	43·7	50·7	54·3	58·2	60·9	63·9	64·7

(*m*-Hydroxyphenyl)diphenylmethanol

Time (min.)	5	10	15	20	30	40	50	60	70
CO_2 (%)	8·70	18·5	21·6	25·1	32·0	36·5	38·4	39·8	41·3

The solution was then cooled and treated with water to precipitate (*m*-hydroxyphenyl)-diphenylmethane. Recrystallized from alcohol, the colourless crystals had m. p. and mixed m. p. 105°.

Action of Sodium on the Alcohol.—(*m*-Hydroxyphenyl)diphenylmethanol (0·276 g.) was dissolved in boiling xylene (75 ml.) in the presence of sodium (0·05 g.). The volume of hydrogen evolved (21·2 ml. at N.T.P.) corresponds to the formation of the disodium derivative. The solution remained colourless throughout, and the disodium derivative was deposited on cooling (Found: Na, 13·5.—Calc. for $C_{19}H_{14}O_2Na_2$: Na, 14·4%).

Rate of Reduction [8] *of* (m-*Hydroxyphenyl*)*diphenylmethyl Chloride*.—A solution of the chloride

[6] Bowden and Jones, *J.*, 1928, 1149.
[7] Baeyer, *Annalen*, 1907, **354**, 167.
[8] Part XII, *J.*, 1940, 1249.

(0·501 g.) in freshly dried bromobenzene (10 ml.) was agitated with molecular silver (1 g.) at 18·5°, and the oxygen absorbed was measured at intervals:

Time (min.)	2	6	10	15	20	30
O_2 absorbed (% at N.T.P.)	43·6	79·1	85·5	89·0	93·0	96·0

Stability of Radical Solutions.—Freshly recrystallized (*m*-hydroxyphenyl)diphenylmethyl chloride (0·05 g.), molecular silver (0·4 g.), and benzene were introduced into a constricted test-tube from which the air had been displaced by dry nitrogen. The tube was sealed, covered with black paper, and shaken for 30 min. to reduce the chloride to the free radical. Two such solutions were prepared, and the optical densities were measured by means of a photoelectric colorimeter with an Ilford OB2 filter. One solution was stored in the dark, while the other was exposed to diffused sunlight. The optical densities (*D*) of the two solutions after various periods are annexed. Benzene solutions of pure (*m*-hydroxyphenyl)diphenylmethyl are thus fairly stable at room temperature in the dark.

Time (hr.)	0	0·5	3	20	24	44	48	72
Temperature (°)	19·5	19·8	19·8	18·0	18·2	19·8	18·8	18·0°
D, dark	32·2	32·4	32·3	31·0	31·0	32·1	13·8	31·1
D, sunlight	38·0	35·0	33·2	32·0	28·0	19·0	14·4	14·7

Dissociation of Di-(m-*hydroxyphenyl*)*tetraphenylethane.*—The degree of dissociation of di-(*m*-hydroxyphenyl)tetraphenylethane in benzene was determined by the indirect cryoscopic method. The chloride was freshly prepared, and both the solvent and the molecular silver were rigorously dried before use. In view of the photosensitivity of the radical, precautions were taken to prevent undue exposure of the solution to light during the measurements. Summarized results are tabulated. After each set of determinations, the solution retained the characteristic colour of the free radical, and gave a normal yield of peroxide on exposure to air.

Degree of dissociation of di-(m-*hydroxyphenyl*)*tetraphenylethane.*

M of radical = 259·3. *M* of the ethane = 518·6.
Cryoscopic const. of benzene = 52·5.
Wt. of solvent = 20·35 g. Wt. of silver = 5·0 g.

Chloride (g.)	Ethane (g.)	Concn. (%)	Δ	*M*	Dissn. (%)	Chloride (g.)	Ethane (g.)	Concn. (%)	Δ	*M*	Dissn. (%)
0·5162	0·4540	2·18	0·303°	386·7	34·1	0·5090	0·4477	2·15	0·302°	382·4	35·6
0·5034	0·4428	2·13	0·292	391·2	32·6	0·6915	0·6082	2·91	0·402	390·3	32·9
0·9388	0·8258	3·90	0·552	386·0	34·4	0·9935	0·8738	4·11	0·567	397·6	30·4

Isolation of Di-(m-*hydroxyphenyl*)*tetraphenylethane.*—(*m*-Hydroxyphenyl)diphenylmethyl chloride (3 g.) in benzene (50 ml.) was shaken with molecular silver (8 g.) for 2 hr. in a Schlenk tube covered with black paper. The solution was filtered into the isolation unit (Part XIV) and evaporated *in vacuo* in a slow stream of carbon dioxide at $>40°$. The residual oil solidified on repeated trituration with light petroleum. The solid was dissolved in the minimum amount of acetone and was cooled with ice until crystallization was complete. The mother-liquor was decanted, and the pale yellow crystals washed with the cold solvent and dried *in situ* in a stream of carbon dioxide. The ethane had m. p. 112—115° (decomp.: vac.).

TATEM LABORATORIES,
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856. *Free Radicals and Radical Stability. Part XVIII.* (Halogenophenyl)diphenylmethyls and the Removal of Nuclear Halogen by Silver.*

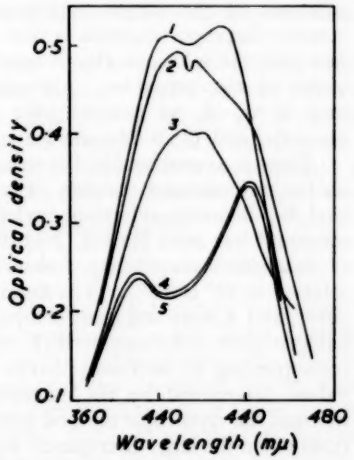
By K. I. Beynon and S. T. Bowden.

In contrast to *para*-substitution, *meta*-substitution by halogen in the triphenylmethyl cation leads to a slight hypsochromic shift in the absorption spectrum.

(*m*-Halogenophenyl)diphenylmethyl chlorides do not form fuchsones, and are reduced to primary radicals which may be isolated in the solid state as the ethanes. The large difference between the values of the unimolecular stability determined by the cryoscopic and the magnetic-susceptibility method is ascribed to incorrect estimation of the diamagnetic contribution in triarylmethyl systems.

Silver removes half of the halogen from (*p*-bromophenyl)diphenylmethyl, but has no action on a radical with *meta*-halogen. This behaviour is interpreted without assuming the existence of a *para*-quinonoid form of the radical.

To ascertain the effects of halogen substituents on the optical properties of the triphenylmethyl cation we have examined the absorption spectra of solutions of the carbinols in sulphuric acid (see Figure). The absorption curves of the *m*-chloro- and *m*-iodo-substituted



Absorption spectra in 98% H_2SO_4: (1) *Triphenylmethanol*; (2) (m-*fluorophenyl*)-, (3) (m-*bromophenyl*)-, (4) (3 : 5-*dibromo-2-methoxyphenyl*)-, *and* (5) (5-*bromo-2-methoxyphenyl*)-*diphenylmethanol.*

ions have a peak and a shoulder [1] whereas those of the corresponding fluoro- and bromo-derivatives have two maxima as indicated in Table 1. The slight hypsochromic shift in the spectrum appears to be a characteristic feature of *meta*-substitution, and is in marked contrast to the bathochromic effect accompanying *para*-substitution. The

Table 1.

R in ion CPh_2R	$\lambda_{max.}$ (mμ)	$10^4\varepsilon_{max.}$	R in ion CPh_2R	$\lambda_{max.}$ (mμ)	$10^4\varepsilon_{max.}$
Ph	408, 431	3·8	*m*-C_6H_4I	422	4·1
m-C_6H_4F	410, 418	3·4	2 : 5 : 1-MeO-C_6H_3Br	392, 442, 552	3·0
m-C_6H_4Cl	416	4·0	2 : 3 : 5 : 1-MeO-$C_6H_3Br_2$	392, 442, 555	3·8
m-C_6H_4Br	411, 422	3·4			

* Part XVII, preceding paper.

[1] Evans, Jones, and Osborne, *Trans. Faraday Soc.*, 1954, **50**, 470.

substitution of methoxyl in the *ortho*-position of the *meta*-halogenated rings leads to a bathochromic shift and separation of the absorption bands.[2]

The influence of halogen substituents on the basicity of the alcohols and the halochromic properties of the salts is indicated in Table 2. It is evident that *meta*-substitution

TABLE 2.

R in CPh_2R	Basicity	Sulphate	R in CPh_2R	Basicity	Sulphate
Ph	1·0	Yellow	*m*-C_6H_4Br	1·3	Yellow
m-C_6H_4F	1·2	Yellow	*p*-C_6H_4Br	—	Yellowish-red
p-C_6H_4F	1·9	Reddish-yellow	2 : 5 : 1-MeO·C_6H_2Br	1·3	Green
o-C_6H_4Cl	1·2	Yellow	2 : 3 : 5 : 1-MeO·$C_6H_2Br_3$	1·3	Green
p-C_6H_4Cl	1·8	Orange-yellow			

leads to a slight increase in the basicity and that *p*-fluorine is the most effective halogen substituent. The fact that the introduction of methoxyl into a (bromophenyl)diphenylmethanol produces little change in the basicity furnishes a further example of the clashing influences which arise when more than one substituent is present. Of the substituents in triphenylmethyl sulphate, hydroxyl is the most effective in reducing hydrolysis. The *p*-methoxyl group enhances the stability, but in the *meta*-position it has practically the same effect as the fluorine and bromine.

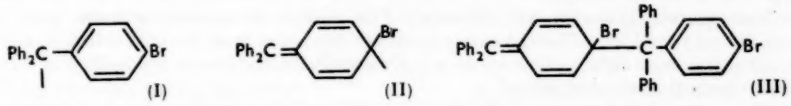
Acetyl chloride converts the (*m*-halogenophenyl)diphenylmethanols into stable chlorides which in non-ionizing solvents are rapidly reduced by molecular silver to the primary radicals. Benzene solutions of (*m*-fluorophenyl)- and (*m*-bromophenyl)-diphenylmethyl retain their colour in the dark for 3 days, and the slight loss of colour which occurs in solutions of the (bromomethoxyphenyl)diphenylmethyls indicates that even in these systems disproportionation is slow under these conditions. This is substantiated by the fact that the solutions absorb nearly the theoretical amount of oxygen, and give normal yields of the peroxides. Although di-*m*-bromophenyltetraphenylethane was obtained only as an oil, we isolated solid ethanes from (*m*-fluorophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl.

There is a considerable difference of opinion regarding the effect of halogen substituents on the unimolecular stability of triphenylmethyl. We found by the cryoscopic method that di-*p*-fluorophenyltetraphenylethane is dissociated to the extent of 20% in 2% benzene solution,[3] but later Marvel, Johnston, Meier, Mastin, Whitson, and Himel [4] on the basis of magnetic-susceptibility measurements reported that the dissociation in a similar solution at 25° is 3·5%. The fluorine atom in this radical, however, is slowly removed by silver, and a more stringent comparison of the two methods is now possible with the (*m*-halogenophenyl)diphenylmethyls which are not attacked by the metal. For the ethanes corresponding to (*m*-fluorophenyl)- and (*m*-bromophenyl)-diphenylmethyl the dissociation values determined by the magnetic-susceptibility method at 25° are 5·8% and 7·0%, whereas the cryoscopic method gives 46% and 43%, respectively. In view of the precautions taken the large discrepancy is probably due to the incorrect evaluation of the diamagnetic contribution in triarylmethyl systems, as has been pointed out by Selwood and Dobres.[5] According to Marvel, Dietz, and Himel [6] substitution of fluorine, chlorine, or bromine in the *meta*- or *para*-positions or of iodine in the *para*-position of one of the rings of triphenylmethyl does not materially alter the radical stability, but such a conclusion is surprising in view of the known effects of halogen substituents in other systems [7] which would be expected to be less sensitive to inductive and mesomeric effects. The present

[2] Deno, Jaruzelski, and Schriesheim, *J. Org. Chem.*, 1954, **19**, 159.
[3] Bowden and Watkins, *J.*, 1940, 1249.
[4] Marvel, Johnston, Meier, Mastin, Whitson, and Himel, *J. Amer. Chem. Soc.*, 1944, **66**, 914.
[5] Selwood and Dobres, *ibid.*, 1950, **72**, 3860.
[6] Marvel, Dietz, and Himel, *J. Org. Chem.*, 1942, **7**, 392.
[7] Baddeley and Bennett, *J.*, 1933, 263; Bird and Ingold, *J.*, 1938, 918; Ingold, *Chem. Rev.*, 1934, **15**, 225; Branch, Yabroff, and Bettmann, *J. Amer. Chem. Soc.*, 1934, **56**, 937, 2568; Dippy, *Chem. Rev.*, 1939, **25**, 176.

work, however, indicates that *m*- and *p*-halogen considerably stabilize the unimolecular system, and that similar influences would operate strongly with *ortho*-substituents, whose inhibiting effect on the association to the ethane is ascribed by Marvel *et al.*[6] to steric factors.

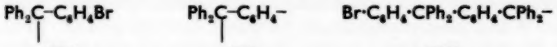
It is now established that nuclear halogen is removed from (halogenophenyl)diphenylmethyl systems by silver. In a further examination of the reaction between (*p*-bromophenyl)diphenylmethyl chloride and the metal, we find that all the chlorine is rapidly lost, and half the total bromine slowly, at room temperature. The theory proposed by Gomberg [8] to account for the latter reaction requires that the halogen is not removed when attached to a benzenoid nucleus but only when the carbon–halogen bond simulates an aliphatic linkage. It is further assumed that the removal of chlorine from (*p*-bromophenyl)diphenylmethyl chloride leads to the benzenoid radical (I) which tautomerizes to



(I) (II) (III)

the quinonoid form (II) and that the two modifications combine to produce (III) in which one of the bromine atoms simulates an aliphatically combined halogen, and is thus removable by silver. Implicit in this argument is the supposition that the two structures (I and II) of the primary radical exist as independent entities, but on the basis of the wave-mechanical theory of free radicals [9,10] it is clear that these forms are actually two of the canonical structures which contribute to the existence of (*p*-bromophenyl)diphenylmethyl as a unimolecular entity.

In view of these considerations and the fact that quinonoid forms of the triarylmethyls have never been isolated, we interpret the reaction as follows: Reduction of (*p*-bromophenyl)diphenylmethyl chloride yields the hybrid radical (IV) in which, for simplicity, the uncoupled electron is represented by a localized free bond. The redistribution of charge density is greatest in *para*- and least in *meta*-positions, and is accompanied by concomitant changes in the polarity of the linkages attaching substituents to the phenyl



(IV) (V) (VI)

nuclei. Owing to the enhanced reactivity of the *para*-bromine atom the metal is now able to attack the primary radical with formation of the diradical (V). The latter combines with the primary radical to form the secondary radical (VI), and the ensuing change in the polarity of the C–Br linkage now renders the molecule resistant to attack by the metal. If we assume that combination of the primary radical with the diradical is faster than the reaction between the primary radical and silver, it follows that only half the total bromine will be removed from the system, as is found experimentally.

The free radicals (*m*-fluorophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl are not attacked by silver at room temperature, and bromine is not removed from (*m*-bromophenyl)diphenylmethyl even when the solution is agitated with the metal at 70° for 3 days. The inertness of *m*-halogen towards silver is to be expected inasmuch as the charge redistribution in the radical does not lead to the requisite activation as it does in the *para*-position.

The present hypothesis is thus able to account for the differences in the reactivity of *para*- and *meta*-substituted radicals towards silver, and for the apparently anomalous behaviour of (*p*-fluorophenyl)diphenylmethyl [3] which cannot be interpreted on the basis of the Gomberg theory.

[8] Gomberg, *J. Amer. Chem. Soc.*, 1914, **36**, 1157.
[9] Burton and Ingold, *Proc. Leeds Phil. Soc.*, 1929, **1**, 421.
[10] Pauling and Wheland, *J. Chem. Phys.*, 1933, **1**, 362; 1934, **2**, 482.

Experimental

(m-*Fluorophenyl*)*diphenylmethanol*.—To *m*-fluorophenylmagnesium bromide prepared from *m*-fluorobromobenzene (23 g.), magnesium (3·5 g.) and ether (50 ml.), a solution of benzophenone (15 g.) in benzene (50 ml.) was added, and the mixture was heated under reflux for 4 hr. The product was hydrolyzed, and volatile material was removed in steam. The solid residue was dissolved in ether, and the solution was warmed with activated charcoal, filtered, and cooled. The deposited methanol (20 g.) was colourless, and had m. p. 118°; Marvel *et al.*[4] give m. p. 117°.

(m-*Fluorophenyl*)*diphenylmethane*.—The alcohol was heated with zinc dust and acetic acid on a steam-bath for 1 hr., and the filtered solution was poured into water to precipitate the methane. Recrystallized from alcohol, it melted at 95° (Found: C, 87·9; H, 5·7. Calc. for $C_{19}H_{15}F$: C, 87·0; H, 5·7%).

(m-*Fluorophenyl*)*diphenylmethyl Chloride*.—The alcohol (5 g.) was warmed with acetyl chloride (10 ml.) for 1 hr. The chloride was slowly deposited from the cold solution, and after recrystallization from light petroleum in a dry atmosphere, the compound melted at 113·5° in agreement with the recorded value.[4]

(m-*Fluorophenyl*)*diphenylmethyl Peroxide*.—A 10% solution of the chloride in benzene was shaken with molecular silver for 2 hr. in the dark. The yellow solution was decanted and the radical oxidized by exposure to air. The crystalline peroxide was washed successively with light petroleum and boiling acetone, and had m. p. 173°. Marvel *et al.*[4] report m. p. 174°.

(m-*Bromophenyl*)*diphenylmethanol*.—This compound has been obtained as an oil by several workers.[6,11] A solution of phenylmagnesium bromide [from bromobenzene (93 g.), magnesium (25 g.), and ether (200 ml.)] was filtered and concentrated to about one-third bulk. After addition of benzene (100 ml.) and then freshly distilled methyl *m*-bromobenzoate (30 g.) in benzene (100 ml.), the solution was boiled for 4 hr., decomposed with ice and dilute sulphuric acid, and distilled in steam. The residual alcohol was treated with charcoal in ether and recovered as an oil which solidified during 6 months, and after several recrystallizations from light petroleum was colourless, m. p. 62·5° (Found: C, 65·0; H, 5·4; Br, 24·6. Calc. for $C_{19}H_{15}OBr$: C, 67·3; H, 4·5; Br, 23·6%).

(m-*Bromophenyl*)*diphenylmethyl Peroxide*.—Prepared in the same way as the corresponding fluorine compound, this melted at 172°; Gomberg and Van Slyke [11] report m. p. 170°.

(5-*Bromo*-2-*methoxyphenyl*)*diphenylmethanol*.—The *alcohol*, prepared from methyl 5-bromo-2-methoxybenzoate [12] and phenylmagnesium bromide, had m. p. 123° (from light petroleum) (Found: C, 65·0; H, 4·8; Br, 21·9. $C_{20}H_{17}O_2Br$ requires C, 65·1; H, 4·6; Br, 22·0%). It gave the *methane*, m. p. 100° (Found: C, 67·4; H, 4·7; Br, 21·9. $C_{20}H_{17}OBr$ requires C, 68·0; H, 4·9; Br, 22·6%), *chloride*, m. p. 116° (Found: Cl, 9·2. $C_{20}H_{16}OClBr$ requires Cl, 9·2%), and *peroxide*, m. p. 153° (Found: C, 64·5; H, 4·4; Br, 19·7. $C_{40}H_{32}O_4Br_2$ requires C, 65·2; H, 4·3; Br, 21·7%).

(3 : 5-*Dibromo*-2-*methoxyphenyl*)*diphenylmethane*.—The alcohol [13] was reduced by the general method. The methane (from alcohol) had m. p. 89° (Found: C, 55·1; H, 3·5; Br, 37·9. Calc. for $C_{20}H_{16}OBr_2$: C, 55·6; H, 3·7; Br, 37·0). The *chloride*, recrystallized from light petroleum–acetyl chloride, had m. p. 111·5—112° (Found: Cl, 7·7. $C_{20}H_{15}OClBr_2$ requires Cl, 7·6%).

Absorption Spectra of the Triarylmethyl Cations.—Solutions of the alcohols in 98% sulphuric acid [(*m*-fluorophenyl)-, 1·44, (*m*-bromophenyl)-, 1·18, (5-bromo-2-methoxyphenyl)-, 1·12, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethanol, $0·91 \times 10^{-5}$ mole/l.] were examined by means of a Unicam S.P. 500 spectrophotometer (see Figure, and Table 1). The curves for the two methoxyl-substituted derivatives show an additional peak at 592 mμ corresponding to optical density 0·08. There was no change in the spectra in 24 hr. in the dark.

Basicity of the Alcohols.—The basicities recorded in Table 2 were determined by Baeyer and Villigers's method.[14]

[11] Cone and Long, *J. Amer. Chem. Soc.*, 1906, **28**, 524; Gomberg and Van Slyke, *ibid.*, 1911, **33**, 181; Tschitschibabin, *Ber.*, 1911, **44**, 458.
[12] Hirwe and Patil, *Proc. Indian Acad. Sci.*, 1939, **5A**, 321.
[13] Kauffmann and Egner, *Ber.*, 1913, **46**, 3786.
[14] Baeyer and Villiger, *Ber.*, 1902, **35**, 1189.

Reduction of (m-*Halogenophenyl*)*diphenylmethyl Chlorides.*—A solution of (*m*-fluorophenyl)-diphenylmethyl chloride (0·428 g.) in bromobenzene (10 ml.) with molecular silver (3·0 g.) at 19° absorbed 1 mol. of oxygen in <15 min. (*m*-Bromophenyl)diphenylmethyl chloride is also rapidly and completely reduced to the free radical under these conditions.

Stability of the Radical Solutions.—No change in optical density (photoelectric colorimeter) occurred when benzene solutions were kept in the dark for 3 days. The volume of oxygen absorbed showed that there was no appreciable disproportionation or isomerization during the period (2—3 hr.) required for the molecular-weight determinations.

Degree of Dissociation of the Ethanes.—The indirect cryoscopic method [15] (benzene solutions of the radicals) gave the results in Table 3. The solvent (20·35 g.) (K = 52·5°) was introduced into the cryoscopic vessel by means of a pipette. 5·0 g. of molecular silver were employed in each series of determinations.

Isolation of Halogenohexaphenylethanes.—Preparation of the free radical and isolation of the corresponding ethane from solution were carried out as described in Part XIV. Di-(*m*-fluorophenyl)tetraphenylethane was a yellowish-brown solid, m. p. 117—121° (decomp.). Di-(*m*-

TABLE 3.

(m-*Fluorophenyl*)*diphenylmethyl.*					(m-*Bromophenyl*)*diphenylmethyl.*				
M of radical = 261·3.			M of ethane = 522·6.		M of radical = 322·2.			M of ethane = 644·4.	
Chloride (g.)	Radical (g.)	Δ	M	Dissocn. of ethane (%)	Chloride (g.)	Radical (g.)	Δ	M	Dissocn. of ethane (%)
0·5092	0·4483	0·315	367·2	42·3	0·7451	0·6714	0·395	438·5	47·0
0·7968	0·7015	0·490	369·3	41·5	1·0227	0·9127	0·535	444·4	44·5
0·5592	0·4923	0·353	359·8	45·3	0·6003	0·5409	0·303	460·6	39·9
0·7636	0·6716	0·501	345·8	51·1	0·8947	0·8060	0·467	445·2	44·7
0·5232	0·4607	0·326	364·7	43·3	0·8665	0·7807	0·436	461·9	39·5
0·7620	0·6710	0·501	345·5	51·3	0·9464	0·8527	0·497	442·6	45·6

bromophenyl)tetraphenylethane was a brown oil, but gave the solid peroxide. Di-(5-bromo-2-methoxyphenyl)tetraphenylethane crystallized at −68°; it was yellowish-brown and melted at 135—139° (decomp.). Di-(3 : 5-dibromo-2-methoxyphenyl)tetraphenylethane separated as pale orange-yellow crystals, m. p. 138—142° (decomp.).

Action of Silver on (*Halogenophenyl*)*diphenylmethyls.*—Bromobenzene solutions containing known amounts of the (halogenophenyl)diphenylmethyls were agitated with molecular silver as usual: the volume of oxygen absorbed and amount of silver halide formed were measured periodically.

In agreement with Gomberg and Blicke [16] we found that with (*p*-bromophenyl)diphenylmethyl absorption fell in 7 days to about 50% of the original value while the radical lost half its halogen.

In experiments with (*m*-fluorophenyl)diphenylmethyl, four specimens were used. The tubes were charged under dry nitrogen with a known weight of the chloride, molecular silver (1·00 g.), and dry bromobenzene (9 ml.), then sealed, covered with black paper, and agitated (see Table 4). The contents of the last four tubes were examined for silver fluoride by the following procedure. Steam was passed through the mixture to remove bromobenzene, and

TABLE 4.

Time	Sample	Chloride (g.)	O_2 absorbed (%)	Time	Sample	Chloride (g.)	O_2 absorbed (%)
20 min.	A	0·4006	99·9	8 hr.	D	0·3894	98·5
1 hr.	A	0·3998	100·8	17 hr.	C	0·5230	97·0
4 hr.	B	0·3854	100·9	74 hr.	C	0·3392	96·5
4 hr.	C	0·3426	98·4	6 days	C	0·5828	95·8
4 hr.	A	0·3602	98·5	10 days	B	0·3916	94·9

the residual mass was boiled with water (150 ml.) before filtration. The filtrate was reduced to small bulk. Addition of lead chloride did not precipitate lead chlorofluoride, and the zirconium–alizarin test for fluoride was negative. Therefore, fluorine is not removed by silver and the fall in oxygen absorption is due to disproportionation or isomerization of the radical.

[15] Part II, *J.*, 1939, 33.
[16] Gomberg and Blicke, *J. Amer. Chem. Soc.*, 1923, **45**, 1768.

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In similar experiments (*m*-bromophenyl)-, (5-bromo-2-methoxyphenyl)-, and (3 : 5-dibromo-2-methoxyphenyl)-diphenylmethyl lost no halogen in 7 days at room temperature. The fluorescein and the fuchsin test for bromide showed that the halogen is not removed from (*m*-bromophenyl)diphenylmethyl at 70° in 3 days.

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857. *The Partial Molar Heats of Solution of Water in Dinitrogen Pentoxide Solutions and of Potassium Nitrate and Sulphuric Acid in Nitric Acid at 0°.*

By L. LLOYD and P. A. H. WYATT.

Specific heats and partial molar heats of solution of water are reported for dinitrogen pentoxide solutions in the range 78·8—89·5% N_2O_5. For potassium nitrate and sulphuric acid, specific heats and heats of solution have been determined up to concentrations of about 2 molal in pure nitric acid.

The derived values of the differential heat of dilution of nitric acid for the solutes water, dinitrogen pentoxide, and potassium nitrate are at variance with the results expected from a simple solvent dissociation involving dissociation products of fixed solvation number.

ON the basis of spectroscopy [1] and cryoscopy [2,3] it is generally accepted that the main dissociation of nitric acid is represented by the equation

$$2HNO_3 \qquad NO_2^+ + NO_3^- + H_2O$$

By treating deviations from Raoult's law in chemical terms, some details have been added to this conclusion. Thus, water is said to be almost unprotonated [4] and dinitrogen pentoxide completely dissociated [1,2] in dilute solutions, whilst all the products of dissociation are regarded as being more or less solvated with nitric acid molecules. The nitrate ion has been assigned a solvation number of 2,[5] and water a solvation number of 1,[4] or perhaps 2 [2,6] near the composition of pure nitric acid.

Since these solvation numbers were calculated on the assumption that deviations from ideality may be treated chemically, the partial molar heats of solution of the dissociation products should depend upon the concentration in a characteristic way.[7] For, if it is assumed that the degree of solvation does not vary markedly with concentration (this has been assumed over considerable concentration ranges for the nitrate ion [5] and water [4,8]), the partial molar heats of solution of water, dinitrogen pentoxide, or an alkali-metal nitrate should decrease with increasing concentration, but tend towards a constant value as the solvent dissociation is suppressed. Further, the derived partial molar heat content of the solvent should tend towards the *same* constant value for all three solutes at high concentrations.

As the existing data on heats of solution in nitric acid are too few near the composition

[1] Ingold and Millen, *J.*, 1950, 2612.
[2] Gillespie, Hughes, and Ingold, *J.*, 1950, 2552.
[3] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.
[4] Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722.
[5] Chédin and Vandoni, *ibid.*, 1948, **227**, 1232.
[6] Fénéant and Chédin, *ibid.*, 1956, **243**, 41.
[7] Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 806.
[8] Chédin, *J. Chim. phys.*, 1952, **49**, 109.

of the pure acid to apply this test, we have made some new measurements on the partial molar heats of solution (at 0°) of potassium nitrate and sulphuric acid in pure nitric acid, and on the partial molar heat of solution of water in dinitrogen pentoxide solutions at concentrations on both sides of the composition of the pure acid. Apart from measurements on the solute water at 20° by Leclerc and Chédin,[9] which have already been interpreted in the way outlined above,[7] a number of determinations of heats of solution at isolated concentrations have been recorded and used to interpret the constitution of nitric acid solutions.[2] But the latter interpretations have been based upon the *total* value of the heat of solution, whilst for the present purposes attention is directed to the *variation* of the heat of solution with composition, which clearly requires a more extensive set of measurements.

Experimental

The 1-pint Pyrex Dewar flask used as a calorimeter was stoppered at the mouth with a Polythene bung, bored to carry five tubes. A short tube in the centre of the bung terminated at its upper end in a B14 joint, into which a tube carrying the thermocouples could be fitted: this extended to within a few mm. of the bottom of the Dewar flask and was closed at its lower end. Around this central tube were grouped a glass cooling " finger," into which pieces of solid carbon dioxide could be dropped to cool the contents of the calorimeter; a tube carrying the electrical heater for specific-heat measurements; a B10 socket, into which a device for adding solids or liquids could be fitted; and a long tube sealed at its upper end in which the arm of a magnetic stirrer could slide freely. This stirrer was similar to that used in vapour-pressure[10] and cryoscopic [3, 11] work. When measurements were about to be made the Polythene bung was always wired into position and greased externally so that the calorimeter was air-tight, and the whole calorimeter was surrounded by a metal jacket rising above the level of the cap so that it could be immersed in an ice-bath without direct contact with moisture.

Five copper–constantan thermocouple junctions, insulated from each other and embedded in naphthalene in a thin-walled glass tube, enabled temperature measurements to be made to within 0·001° when used in conjunction with a Cambridge Vernier Potentiometer. Since the temperature changes to be recorded were of the order of 1°, this degree of precision was quite sufficient to ensure that temperature errors were not limiting. (The overall experimental error was of the order of 1%, most of which probably arose from the fact that the surroundings of the ice-bath were at room temperature.) The ice-point, the sodium sulphate hydrate transition at 32·388°, and the freezing point of sulphuric acid [11, 12] were used in calibrating the thermocouples. A separate Dewar flask containing pure ice was immersed in the ice-bath alongside the calorimeter and housed the cold junctions.

The heating element, consisting of a small coil of resistance wire constructed so that it would produce a temperature rise in the calorimeter of about 0·6° in 10 min., was immersed in transformer oil in a thin-walled glass tube, the main length of which was packed with wax around the leads. Two copper leads were silver-soldered at each end of the heating coil, one pair serving to carry the heating current and the other to tap off the potential drop across the heater. Before the heater was switched on, the potential source (two 90 ampère-hour 2-volt accumulators in parallel) was always connected through an identical resistance coil (the " ballast ") for about an hour to stabilize the potential. During a heating period the observed potential drop across the heater never changed by more than 0·05%, and the heat input was calculated from the average potential drop, the time, and the resistance of the heater, which was calibrated by comparison with a standard 1 ohm resistance.

When a measurement was to be made, nitric acid was weighed into the calorimeter at about −5°, after which the calorimeter was sealed and kept in the ice-bath for at least 1 hr. As the temperature approached 0°, readings were taken every minute for a period of 8—10 min. to establish the rate of leakage before heating. Then either the electrical heater was switched on or an addition of solute was made, after which further readings were taken at intervals of 1 min.

[9] Leclerc and Chédin, *Mém. Services chim. État*, 1945, **32**, 87.
[10] Lloyd and Wyatt, *J.*, 1955, 2248.
[11] Gillespie, Hughes, and Ingold, *J.*, 1950, 2473.
[12] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 297.

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to establish the rate of leakage after the change of temperature By extrapolating the readings for the pre- and post-periods to the time when the temperature of the calorimeter had risen half-way to the final temperature, a corrected value of the temperature rise was obtained. A correction was made for the temperature of the added solute, which was measured by a single-junction thermocouple in the adding device.

A further complication is introduced by the variability of the water equivalent of a Dewar flask with the extent to which it is filled.[13] The calorimeter used had a water equivalent which varied from 25·8 g. when it contained 140 g. of water to 34·4 g. when it contained 230 g. To find the volume of liquid, nitric acid solutions being unstable, the density of some solutions was determined with a form of pyknometer which permitted rapid reading; this consisted of a glass bulb and stem with a total capacity of about 10 c.c. The stem was graduated and could be read to 0·001 c.c., so that, after calibration with water at various points on the scale and at different temperatures, the volume of a known weight of solution could always be read without the necessity for adjusting the meniscus to a fixed mark at each temperature.

Materials.—The dinitrogen pentoxide solutions and pure nitric acid were prepared by standard methods,[10] and the sulphuric acid cryoscopically. Potassium nitrate was " AnalaR."

Results

The results for the partial molar heats of solution are collected in Tables 1, 2, and 3, and those for specific heats and densities in Tables 4, 5, and 6. Specific-heat measurements were

Table 1. *Partial molar heats of solution of water in dinitrogen pentoxide solutions at* 0°, *and the derived differential heats of dilution of nitric acid.*

N_2O_5 (% by wt.)	H_2O (m)	N_2O_5 (m)	$\frac{m_{H_2O}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{H_2O}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$	N_2O_5 (% by wt.)	H_2O (m)	N_2O_5 (m)	$\frac{m_{H_2O}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{H_2O}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$
89·5	−2·34	1·80	−0·147	5897	−532·9	85·5	0·11	—	0·007	3176	—
89·2	−2·19	1·72	−0·138	4984	−402·6	$85·3_5$	0·22	—	0·014	3368	7·3
88·8	−1·93	1·54	−0·122	3976	−271·8	85·2	0·28	—	0·018	3575	10·5
88·4	−1·72	1·41	−0·108	2998	−159·3	84·9	0·56	—	0·035	3986	21·6
88·0	−1·46	1·24	−0·092	2206	− 80·1	84·5	0·85	—	0·054	4124	27·7
87·5	−1·14	1·00	−0·072	1423	− 15·9	84·1	1·08	—	0·068	4157	29·7
87·0	−0·82	0·74	−0·052	885	+ 17·5	83·8	1·25	—	0·079	4157	—
86·5	−0·50	0·47	−0·032	857	19·5	83·6	1·42	—	0·090	4198	32·9
86·1	−0·28	0·27	−0·018	1736	—	83·5	1·48	—	0·093	4202	33·2
$86·0_2$	−0·22	0·21	−0·014	1446	6·0	83·2	1·72	—	0·108	4171	30·2
$85·9_6$	−0·17	0·17	−0·011	1582	4·1	80·2	3·86	—	0·244	4141	+24·9
$85·9_3$	−0·11	0·11	−0·007	1769	2·4	79·8	4·18	—	0·264	4029	− 3·6
$85·8_1$	−0·06	0·06	−0·004	2114	0·5	79·3	4·57	—	0·288	3990	−14·4
$85·6_3$	+0·06	—	+0·004	2626	0·5	78·8	4·90	—	0·309	3836	−60·4

Table 2. *Partial molar heats of solution of potassium nitrate in nitric acid solutions at* 0°, *and the derived differential heats of dilution of nitric acid.*

KNO_3 (m)	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{KNO_3}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$ (cal. mole^{-1})	KNO_3 (m)	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\bar{H}_{KNO_3}$ (cal. mole^{-1})	$\bar{L}_{HNO_3}$ (cal. mole^{-1})
0·10	0·006	6590	—	0·21	0·013	6830	—
0·22	0·014	6770	—	0·83	0·052	6490	−10·5
				1·02	0·064	6330	−19·5
0·03	0·002	6540	—				
0·095	0·006	6690	+1·0	0·32	0·020	6840	+2·5
0·35	0·022	6650(?)	—	1·50	0·094	6200	−28·8
0·51	0·032	6810	+2·4	1·57	0·099	6140	−33·8
				2·27	0·143	5240	−145

made at definite compositions before and after the addition of solutes: the compositions quoted for the partial molar heats of solution, on the other hand, represent the average of the compositions before and after an addition of the solute. It was assumed that the quantities of solute added were small enough to give a direct estimate of the partial molar heat of solution at this

[13] Kunzler and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 3472.

TABLE 3. *Partial molar heats of solution of sulphuric acid in nitric acid solutions at 0°, and the derived differential heats of dilution of nitric acid.*

H_2SO_4 (m)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\overline{H}_{H_2SO_4}$ (cal. mole^{-1})	$\overline{L}_{HNO_3}$ (cal. mole^{-1})	H_2SO_4 (m)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	$-\overline{H}_{H_2SO_4}$ (cal. mole^{-1})	$\overline{L}_{HNO_3}$ (cal. mole^{-1})
0·05	0·003	6750	+0·2	1·11	0·070	4800	−131
0·19	0·012	7070	+2·0	1·78	0·112	3550	−238
0·35	0·022	7360	+7·5	1·91	0·120	3540	−241

TABLE 4. *Specific heats of nitric acid solutions.*

N_2O_5 as solute		N_2O_5 as solute		N_2O_5 as solute		N_2O_5 as solute	
N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	N_2O_5 (%)	C_p (cal. g.$^{-1}$ deg.$^{-1}$)
89·7	0·424	86·7	0·396	85·5	0·415	83·4	0·423
89·3	0·425	86·3	0·404	85·2	0·420	83·0	0·422
89·0	0·413	86·1	0·407	84·6	0·428	80·4	0·448
88·6	0·408	86·0	0·408	84·0	0·426	80·0	0·456
88·2	0·399	85·9	0·410	83·9	0·424	79·5	0·462
87·7	0·392	85·8	0·412	83·7	0·420	79·0	0·465
87·2	0·394	85·7 *	0·413	83·5	0·423	78·6	0·467

* *I.e.*, 100% HNO_3.

KNO_3 as solute		KNO_3 as solute		H_2SO_4 as solute	
$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	C_p (cal. g.$^{-1}$ deg.$^{-1}$)
0·000	0·413	0·037	0·380	0·007	0·412
0·003	0·410	0·060	0·354	0·017	0·422(?)
0·004	0·412	0·092	0·388	0·026	0·414
0·009	0·408	0·096	0·384	0·065	0·419
0·010	0·407	0·102	0·376	0·108	0·422
0·018	0·404	0·142	0·375	0·116	0·423
0·024	0·400	0·283	0·366	0·125	0·425
0·027	0·391				

TABLE 5. *Densities (d) of potassium nitrate–nitric acid solutions (in g. cm.$^{-3}$) at 0°, 10°, and 20°.*

$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}	$\frac{m_{KNO_3}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}
0·000	$1·547_0$	$1·529_3$	$1·513_5$	0·225	$1·732_3$	$1·719_4$	$1·709_0$
0·066	$1·612_0$	$1·596_7$	$1·583_4$	0·283	$1·756_5$	$1·744_0$	$1·733_4$
0·123	$1·661_9$	$1·647_9$	$1·636_0$	0·416	$1·817_8$	$1·806_1$	$1·797_1$

TABLE 6. *Densities (d) of sulphuric acid–nitric acid solutions (in g. cm.$^{-3}$) at 0°, 10°, and 20°.*

$\frac{m_{H_2SO_4}}{m_{H_2O}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}	$\frac{m_{H_2SO_4}}{m_{HNO_3}}\left(\frac{m}{m}\right)$	d_0	d_{10}	d_{20}
0·040	$1·581_9$	$1·565_6$	$1·551_5$	0·273	$1·700_5$	$1·685_4$	$1·673_3$
0·074	$1·609_2$	$1·592_7$	$1·579_0$	0·373	$1·729_3$	$1·714_3$	$1·702_4$
0·174	$1·664_0$	$1·648_0$	$1·634_7$				

average composition. Values of the differential heat of dilution of nitric acid relative to pure nitric acid ($\overline{L}_{HNO_3}$) were estimated by the standard graphical method [14] using the formula

$$\overline{L}_1 = -\int_{m_2=0}^{m_2} (m_2/m_1)\mathrm{d}\overline{H}_2 \qquad (m = \text{molality})$$

Values of this quantity are necessarily very sensitive to the shape of the $\overline{H}_2$ curve, especially as m_2/m_1 tends to zero. Since the points for potassium nitrate were more than usually scattered

[14] Lewis and Randall, "Thermodynamics," McGraw-Hill, New York, 1923, p. 92.

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in this region of composition (probably because it was added as a solid), it is difficult to assess the reliability of the solvent heats of dilution in this case. Nevertheless, the $\overline{L}_{HNO_3}$ values quoted would have to be several hundred per cent. in error to have the slighest effect upon the conclusions drawn in this work.

In the case of the water–dinitrogen pentoxide system, the specific heat was studied in detail in the neighbourhood of the composition of 100% nitric acid (85·7% N_2O_5) in order to see if a maximum occurred at this point, as has been recorded for 100% sulphuric acid.[13] Our observations show that no such maximum occurs at 0°, although a point of inflexion can be detected. Maxima do, however, occur at 84·9% and 89·5% N_2O_5, and minima at about 82% and 87·7% N_2O_5. Comparison with the very accurate determination of the specific heat of pure nitric acid by Forsythe and Giauque,[15] 0·420 cal. g.$^{-1}$ deg.$^{-1}$, suggests that the specific-heat data quoted here are probably low by 1·7% owing to a systematic error. The data were nevertheless used as they stood in the calculation of the heats of solution, since these measurements were made under the same experimental conditions.

Our results for the heats of solution of water agree well as to general trend and order of magnitude with those of Leclerc and Chédin [9] at 20°, but show some differences in detail, particularly between 84 and 85% N_2O_5, where their values are 200—500 cal. mole^{-1} more positive. The fact that our results show far less change in $\overline{H}_{H_2O}$ in the region 80—85% N_2O_5 can probably be explained by the difference in temperature of the measurements, since results showing the same trend as Leclerc and Chédin's can be obtained from the results at 0° and graphical estimates of the partial molar specific heat of water.

Discussion

The differential heats of dilution of nitric acid have been plotted in the Figure. Water is the only one of the solutes which even approximates to the simple behaviour expected from a dissociation product. The curve for dinitrogen pentoxide begins very similarly to that for water, but diverges markedly at relatively low concentrations (~0·6 molal) and shows values of the solvent heat of dilution of hundreds of calories at concentrations less than 2 molal. The initial positive portion of the curve is very much less marked for potassium nitrate, whose behaviour differs considerably from that of water and dinitrogen pentoxide even in dilute solutions, whilst at greater concentrations this solute also produces large negative heats of dilution of the solvent.

If it is accepted that the main dissociation reaction for nitric acid is represented by the equation

$$s\mathrm{HNO_3} \rightleftharpoons \mathrm{H_2O} + \mathrm{NO_2^+} + \mathrm{NO_3^-} + (s-2)(\mathrm{HNO_3\ of\ solvation})$$

the methods described in a former paper [7] can be used to show that it is improbable that even the water curve can be regarded as "ideal." From the differences between the partial heat contents of both the solute and the solvent at the composition of the pure solvent and at concentrations of solute high enough to suppress the solvent dissociation, the following results can be deduced (equations 25 and 29 of ref. 7 being applied to the results of this paper):

$$\Delta_d H \,.\, as/(a+b) = -1850 \text{ cal. mole}^{-1}$$
$$\alpha_0 \Delta_d H = -33 \text{ cal. mole}^{-1}$$

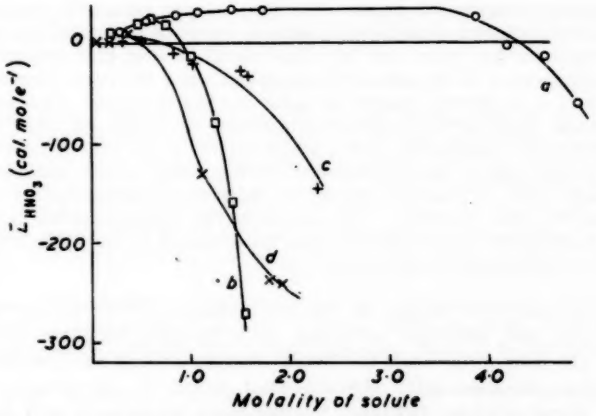
As in ref. 7, $\Delta_d H$ represents the heat of dissociation per mole of solvent, s the total number of molecules of nitric acid involved in the dissociation reaction, a and b the numbers of particles given per molecule of water and dinitrogen pentoxide respectively, and α_0 the fraction of solvent molecules dissociated in pure nitric acid. Combining the two equations, we have $\alpha_0/s = 0{\cdot}018a/(a+b)$, and on substitution of $a = 1$, $b = 2$, α_0/s becomes 0·006. The corresponding value of α_0/s at 0° derived from vapour-pressure determinations [16] is 0·04/3 × 0·96, *i.e.*, 0·014. Further, by applying the van't Hoff isochore, the vapour-pressure results at 0°, 10°, and 20° can be shown to yield a value of the total heat of the

[15] Forsythe and Giauque, *J. Amer. Chem. Soc.*, 1942, **64**, 48.
[16] Lloyd and Wyatt, following paper.

dissociation reaction (*i.e.*, $s\Delta_d H$) which is practically independent of s and is about $-8{\cdot}9$ kcal. mole^{-1}. Thus the vapour-pressure data yield $\alpha_0\Delta_d H = -0{\cdot}014 \times 8900 = -124$ cal. mole^{-1}. That the thermal result is much smaller (-33 cal. mole^{-1}) suggests that the flattening of the partial molar heat content curve for water is probably deceptive, and that a thermal effect of opposite sign to the suppression of solvent dissociation is masking the latter effect even in the case of water.

This opposing thermal effect might, of course, be due to variable solvation, though it is rather unsatisfactory that considerable variation is required in regions of composition for which *fixed* solvation numbers were originally suggested by Chédin and his co-workers to

The relative heat of dilution of nitric acid in the presence of various solutes.



Curve *a*, H_2O; curve *b*, N_2O_5; curve *c*, KNO_3; curve *d*, H_2SO_4.

explain their vapour-pressure data.[4,5] Nevertheless, the thermal changes in these solutions are so large that it seems likely that some form of "chemical" explanation is necessary, as can be seen by comparison with the case of the solute sulphuric acid, in which changes in the extent of conventional chemical reactions are thought to be occurring.[6,16] The simplest chemical explanation for dinitrogen pentoxide would be that it is not a completely strong electrolyte, but such an explanation contradicts the strong Raman evidence [1] for its complete ionisation.

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858. *The Vapour Pressures of Nitric Acid Solutions. Part II.* The Behaviour of Solutes in Nitric Acid.*

By L. Lloyd and P. A. H. Wyatt.

The effects of solutes upon the vapour pressure of 100% nitric acid are reported; apart from some measurements with potassium nitrate at 10° and 20°, all determinations were at 0°. The solutes potassium nitrate, ammonium nitrate, sodium nitrate, phosphoric acid, potassium dihydrogen phosphate, sulphuric acid, potassium sulphate, perchloric acid, ammonium perchlorate, and acetic acid all give solutions which yield no measurable excess of water or dinitrogen pentoxide in the vapour. There is some evidence for the dehydration of orthoboric acid by nitric acid, since the vapour contains an excess of water; acetic anhydride and acetyl nitrate yield vapours containing a marked excess of dinitrogen pentoxide. Since the data for water and the alkali-metal nitrates give straight lines (after suppression of the solvent dissociation) when the partial pressure of nitric acid p is plotted against the solute/solvent molecular ratio (m_2/m_1), provisional values for the numbers of particles (ν) yielded by other solutes are derived by comparison with a graph of this kind. The same form of graph is also used to provide estimates of the extent of self-dissociation of nitric acid at 0°, 10°, and 20°, leading to results in fair agreement with those obtained by other methods. By continuing the vapour-pressure measurements to the limit of saturation, values are obtained for the solubilities of a number of substances in nitric acid.

In view of the success of cryoscopy in the determination of the modes of ionization of solutes in sulphuric acid, attempts have been made to apply the same technique to pure nitric acid.[1,2] The interpretation of the results is more difficult for this solvent, however, as the far greater self-dissociation obscures that region of concentration in which an approximately linear relation between freezing-point depression and solute molality would otherwise be expected. Heats of dilution also complicate the treatment when greater solute concentrations are used. The latter difficulty is by-passed in isothermal measurements; in view of the appreciable volatility of nitric acid at ordinary temperatures, and of the fact that Chédin, Fénéant, and Vandoni [3] were able to represent vapour-pressure results for the solutes water and potassium nitrate in a simple way, we have tried the use of the vapour-pressure technique instead of cryoscopy to investigate the behaviour of other solutes in nitric acid. Although the interpretations of our results are not always entirely satisfactory, sufficient results have been collected to show that this technique can provide useful information.

Further measurements in the region of 100% nitric acid have led us to doubt our suggestion (Part I) that the vapour over pure nitric acid might contain 0·2% excess of water. Fortunately, however, such precision in the composition of the vapour is unnecessary in the present application, for which the vapour composition is clearly so near pure nitric acid that no complications arise in this respect. Nevertheless, data referring to water and dinitrogen pentoxide as solutes used here were obtained from the results in Part I by increasing the N_2O_5 concentration by 0·25%. This correction also gives better agreement with the Duhem–Margules equation and with the experimental results of Vandoni and Laudy.[4]

* Part I, *J.*, 1955, 2248.

[1] Gillespie, Hughes, and Ingold, *J.*, 1950, 2552.
[2] Dunning and Nutt, *Trans. Faraday Soc.*, 1951, **47**, 15.
[3] Chédin, Fénéant, and Vandoni, *Compt. rend.*, 1948, **226**, 1722; **227**, 1232.
[4] Vandoni and Laudy, *J. Chim. phys.*, 1952, **49**, 99.

Experimental

The method for determination of vapour pressures was described in Part I. During over 2 years' use of the apparatus we have observed a slight change (<1%) in the manometer reading obtained for pure nitric acid. This has been ascribed to a slight alteration in the density of the manometer oil, which can be allowed for by occasional calibration with the vapour pressure of the pure acid. After all additions to the cell, which were always made by weight, the solution was repeatedly frozen, pumped, and thawed to remove air as described in Part I.

Materials were " AnalaR." Solids were dried at 105° and stored over concentrated sulphuric acid. Acetic acid was refluxed for 2—3 hr. with chromic anhydride, distilled off, and fractionated (b. p. 117·3—118·2°). Acetic anhydride was fractionated (b. p. 139·0—139·5°). Acetyl nitrate was prepared by adding an equivalent amount of acetic anhydride to dinitrogen pentoxide and cooling until all the crystals of the pentoxide had dissolved. Perchloric acid was used as a solution in nitric acid, prepared by adding the calculated amount of a dinitrogen pentoxide solution to an aqueous solution of perchloric acid. 100% Phosphoric acid was prepared from " AnalaR " (aqueous) phosphoric acid by adding the calculated amount of phosphoric oxide.

Results

In the Tables, m_2/m_1 represents the overall stoicheiometric ratio of the number of moles of solute to the number of moles of solvent present in the cell, irrespective of whether or not all the solute had completely dissolved. The entries marked " (s) " (for " saturated ") show that at that composition some solute remained solid. In some cases it was possible to raise the temperature to dissolve this solid and then to supercool the resultant liquid, giving a supersaturated solution [represented by " (ss) "] of the same overall composition. P represents total vapour pressure, and p the partial pressure of HNO_3 or the total pressure if HNO_3 is the only volatile species.

Determination of Solubilities.—When the solute is a solid, vapour-pressure measurements can be continued to the limit of solubility. Further additions should have a reduced effect upon the vapour-pressure, and no effect at all if the solid phase in equilibrium with the liquid

Table 1. *Vapour pressures of nitric acid over potassium nitrate–nitric acid mixtures at 0°, 10°, and 20°.*

	p (mm. Hg)				p (mm. Hg)				p (mm. Hg)	
m_2/m_1	0°	10°	20°	m_2/m_1	0°	10°	20°	m_2/m_1	0°	10°	20°
0·000	14·02	26·40	47·00	0·099	11·47	21·48	38·56	0·299	7·30 (s)	10·87 (s)	19·05
0·021	13·70	25·46	45·80	0·134	10·25	19·36	34·90	—	5·36 (ss)	10·22 (ss)	—
0·042	13·15	24·68	44·04	0·202	7·84	14·98	27·87	0·347	—	11·10 (s)	15·23 (s)
0·071	12·35	23·14	41·35	0·262	7·23 (s)	12·20	22·25				

Table 2. *Vapour pressures at 0° of some nitric acid solutions having no measurable excess of water or dinitrogen pentoxide in the vapour.*

Solute									
NH_4NO_3	m_2/m_1	0·026	0·056	0·107	0·175	0·244	0·275		
	p (mm. Hg)	13·54	12·87	11·30	9·05	8·78 (s)	8·54 (s)		
$NaNO_3$	m_2/m_1	0·047	0·093	0·114					
	p (mm. Hg)	13·30	12·71 (s)	12·73 (s)					
H_3PO_4	m_2/m_1	0·024	0·059	0·093	0·130	0·160	0·193	0·227	0·289
	p (mm. Hg)	13·64	13·22	12·99	12·85	12·44	12·24	12·20	11·87
	m_2/m_1	0·367	0·442	0·853	1·665				
	p (mm. Hg)	11·44	10·95	8·73	6·83 (s)	6·12 (ss)			
KH_2PO_4	m_2/m_1	0·011	0·036	0·064	0·091	0·121	0·151	0·184	0·208
	p (mm. Hg)	13·79	12·91	11·85	11·00	9·74	8·77	7·30	6·22
H_2SO_4	m_2/m_1	0·030	0·133	0·189	0·249				
	p (mm. Hg)	13·15	11·03	10·13	9·65				
K_2SO_4	m_2/m_1	0·016	0·040	0·070	0·098	0·135	0·155	0·183	
	p (mm. Hg)	13·66	12·09	10·13	8·23	5·92 (s)	5·44 (s)	4·76 (s)	
$HClO_4$	m_2/m_1	0·075	0·099	0·145	0·220	0·308			
	p (mm. Hg)	12·00	11·33	10·44	9·75 (s)	9·34 (s)			
NH_4ClO_4	m_2/m_1	0·009	0·031						
	p (mm. Hg)	13·83	13·54 (s)						

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TABLE 3. *Total vapour pressures of boric acid–nitric acid mixtures at* 0°.

[At higher concentrations, excess of water was detectable in the vapour: the vapour composition at $m_2/m_1 = 0.512$ was 99·4% (by wt.) of nitric acid.]

m_2/m_1	0·018	0·050	0·097	0·148	0·208	0·265	0·322
P (mm. Hg)	13·85	13·30	12·57	11·39	10·22	9·12	7·98
m_2/m_1	0·388	0·452	0·512				
P (mm. Hg)	6·86	6·54 (s)	6·60 (s)	(p = 6·48 mm. Hg)			

TABLE 4. *Total vapour pressures of nitric acid–acetic acid mixtures at* 0°.

[The vapour was found to contain only nitric acid up to a concentration of at least $m_2/m_1 = 0.337$.]

m_2/m_1	0·025	0·060	0·101	0·149	0·215	0·273	0·337		
$m_1/(m_1 + m_2)$	0·975	0·943	0·909	0·871	0·823	0·785	0·748		
P (mm. Hg)	13·70	13·15	12·47	11·75	10·47	9·49	8·35		
$m_1/(m_1 + m_2)$	0·630	0·570	0·489	0·402	0·273	0·296	0·215	0·122	0·000 *
P (mm. Hg)	4·82	3·39	2·12	1·41	1·56	1·53	1·75	2·70	3·63 †

* Pure acetic acid was also found to have a vapour pressure of 12·72 mm. Hg at 20°, and 6·91 mm. Hg when supercooled to 10°. † Supercooled.

TABLE 5. *Total vapour pressures of nitric acid–acetic anhydride mixtures at* 0°.

[The vapour contained excess of dinitrogen pentoxide: at $m_2/m_1 = 0.076$ the vapour contained 88·48% of N_2O_5, indicating a nitric acid partial pressure of 10·29 mm. Hg, and at $m_2/m_1 = 0.122$ the vapour contained 94·5% of N_2O_5, giving p = 9·53 mm. Hg.]

m_2/m_1	0·015	0·045	0·064	0·076	0·101	0·122	0·209	0·285
P (mm. Hg)	13·55	11·91	11·69	12·95	18·13	24·53	33·98	28·26

TABLE 6. *Total vapour pressures of nitric acid–acetyl nitrate mixtures at* 0°.

[The vapour contained excess of dinitrogen pentoxide.]

m_2/m_1	0·035	0·055	0·077	0·084	0·093	0·125	0·157
P (mm. Hg)	13·47	12·99	12·60	12·62	13·27	19·03	27·30

has the same composition as the original solid added. By continuing to plot the overall (solid + liquid) composition on a graph such as Fig. 2, a value for the solubility of the solute can be obtained from the point of intersection of the lines representing the homogeneous and the heterogeneous systems. The solubility values shown in Table 7 were determined in this way.

TABLE 7. *Solubilities* (S, *in g. per* 100 *g. of* HNO_3) *in nitric acid, at* 0° *unless otherwise stated.*

Substance	m_2/m_1 at intersection	S	Substance	m_2/m_1 at intersection	S	Substance	m_2/m_1 at intersection	S
KNO_3.....	0·220	35·0	$NaNO_3$ ...	0·068	9·2	NH_4ClO_4	0·02	3·7
KNO_3 (10°)	0·283	45·1	KH_2PO_4 ...	>0·208	>45	H_3BO_3 ...	0·404	38·4
KNO_3 (20°)	0·339	54·1	K_2SO_4	0·134 *	—	N_2O_5	0·252	44
NH_4NO_3 ...	0·210	26·7						

* Solid phase = $KHSO_4$.

DISCUSSION

Chédin *et al.*[3] have shown that the vapour-pressure data for the solutes water and potassium nitrate can be interpreted by assuming that the solutions are ideal when solvation has been allowed for. When water is ascribed the solvation number 1 and the nitrate ion 2, the data require that each water molecule yields one particle in solution and each potassium nitrate molecule two particles, as would be expected from little ionization of H_2O and complete dissociation of KNO_3. Our thermal measurements [5] and Chédin's more recent considerations [6] indicate that the position cannot be so simple, but this approach provides a basis for classifying the data.

If Raoult's law is obeyed, the mole-fraction of nitric acid in the liquid phase, x, is related

[5] Lloyd and Wyatt, preceding paper.
[6] Chédin, *J. Chim. phys.*, 1952, **49**, 109.

to its partial pressure, p, by the expression $x = p/p^\circ$. When a solute suppresses the self-dissociation of nitric acid, p° must clearly refer to the hypothetical (extrapolated) value of the vapour pressure corresponding to undissociated nitric acid, but when a solute does not affect the dissociation of nitric acid (apart from a dilution effect), we may suppose that the extent of this dissociation will be practically unaffected over a moderate range of concentration, and the measured vapour pressure of pure nitric acid would be the better choice for p° in the ratio p/p°.

Suppose now that a solution is made from m_1 moles of nitric acid and m_2 moles of the solute, and that each molecule of the solute uses s molecules of solvent in solvation and reaction to form ν particles. Then

$$x = (m_1 - sm_2)/(m_1 - sm_2 + \nu m_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

whence

$$x/(1 - x) = (1/\nu)(m_1/m_2) - (s/\nu) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Thus a plot of $x/(1 - x)$ against m_1/m_2 should be a straight line of slope $1/\nu$ and intercept $-s/\nu$, from which both ν and s can be determined. From a plot of p against m_2/m_1 (see

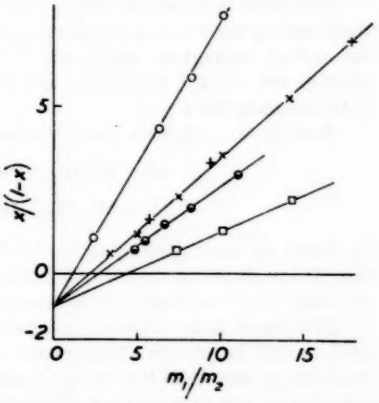

FIG. 1. *The application of Raoult's law to the nitric acid vapour-pressure data.*
○, H_2O; ×, KNO_3; +, NH_4NO_3; ⊖, KH_2PO_4; □, K_2SO_4.

below) for H_2O and KNO_3, the best extrapolated value for p° at 0° seemed to be 14·70 mm. Hg. Using this figure for the calculation of x, we have plotted $x/(1 - x)$ against m_1/m_2 for several solutes (Fig. 1), and obtained values of ν and s/ν shown in Table 8. According to current ideas, acetic acid should be omitted from this group since it is regarded as undergoing no change other than solvation and would not therefore repress the dissociation of the solvent.

TABLE 8. *Application of Raoult's law to the vapour-pressure data.*

Solute	H_2O	KNO_3 and NH_4NO_3	H_3BO_3	KH_2PO_4	K_2SO_4	$CH_3{\cdot}CO_2H$
ν	1·2	2·25	1·51	2·78	4·47	1·4
s/ν	1·0	1·0	1·0	1·0	1·0	0·8
$\nu/1{\cdot}125$	1·1	2·0	1·34	2·5	4·0	1·24

The results for the other compounds in Table 8 not only show ν values rather higher than expected but show a marked tendency to require the same intercept of −1. This must be accidental to some extent, since part at least of the value of s has a very definite meaning when nitric acid is actually removed by reaction (*e.g.*, KH_2PO_4, K_2SO_4, see below). Nevertheless, this observation suggests that it may be profitable to treat the data in other ways than those involving the assumption of solvation. Our present interest, however, is in the determination of plausible ν values, and one obvious approach is demonstrated in the last row of Table 8, where the ν values derived from the slopes in Fig. 1 have been divided by a factor such that the final values for KNO_3 and NH_4NO_3 become 2·0.

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A more direct empirical method follows from the intercepts in Fig. 1 all being about −1. For this implies that $\nu = s$, whence equation (1) can be written as $x = 1 - \nu(m_2/m_1)$, which suggests that the observed partial pressure of nitric acid p should vary linearly with m_2/m_1 and that the slope should depend directly upon ν. In Fig. 2 values of p have been plotted directly in this way, with use of the ν values of 1·0 for H_2O; 2·0 for N_2O_5, KNO_3, and NH_4NO_3, 2·5 for KH_2PO_4; and 4·0 for K_2SO_4. At present, comparison with this diagram provides the simplest method for deriving tentative ν values for other solutes in nitric acid.

For partial pressures of nitric acid p below about 13 mm. at 0°, the following empirical formulæ fit the present results:

$$\nu = (14{\cdot}7 - p)/16{\cdot}4(m_2/m_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

for a solute which suppresses the dissociation of the solvent; and

$$\nu = (14{\cdot}0 - p)16{\cdot}4(m_2/m_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

for a solute which does not suppress the dissociation of the solvent (*e.g.*, acetic acid).

Behaviour of Solutes in Nitric Acid at 0°.—Water and dinitrogen pentoxide are generally supposed to have $\nu = 1$ and 2, respectively. The points for dinitrogen pentoxide in Fig. 2 are rather anomalous over part of the concentration range, though the nearest whole number for ν is 2. Potassium and ammonium nitrates with $\nu = 2$ agree well with water if this is assigned $\nu = 1$.

Boric acid. At least two interpretations are possible:

$$(a) \quad 4H_3BO_3 \longrightarrow H_2B_4O_7 + 5H_2O; \qquad \nu = 1{\cdot}5$$

$$(b) \quad 3H_3BO_3 \longrightarrow (HBO_2)_3 + 3H_2O; \qquad \nu = 1{\cdot}3_3$$

Of these, (*a*) seems the more likely chemically, but $\nu = 1{\cdot}33$ gives better agreement with the other solutes at higher concentrations. Both require the production of water in the solution, which is confirmed by analysis of the vapour (see Table 3).

Phosphoric acid. Since no excess of water was detected in the vapour, orthophosphoric acid cannot be greatly dehydrated in nitric acid solutions. On the other hand, m_2/m_1 must be greater than 0·5 before formation of 1 mole of H_2O per mole of H_3PO_4 could be detected in this way, in view of the low volatility of water in nitric acid solutions stronger than 90% by weight. The ν values, however, which are always less than 1 and decrease towards 0·5 at the highest concentrations, suggest polymerization rather than poly-acid formation with elimination of water, and an equilibrium constant of 10 for the formation of a dimer can be shown to give nitric acid partial pressures which agree with those observed to within 1—2% over the m_2/m_1 range of 0·024—0·442.

Potassium dihydrogen phosphate. The observed ν value of 2·5 could be explained at the higher concentrations by the reaction

$$2KH_2PO_4 + HNO_3 \longrightarrow 2H^+ + 2NO_3^- + 2H_3PO_4$$

since ν for H_3PO_4 then approximates to 0·5. It is probable therefore that phosphoric acid is weak enough for its salts to be completely solvolysed in nitric acid.

Acetic acid, acetic anhydride, and acetyl nitrate. These all appear to behave as would be expected from labile equilibria in the N_2O_5–H_2O–$(CH_3{\cdot}CO)_2O$ system; as acetic acid is the only one of the three that gives no excess of dinitrogen pentoxide in the vapour, we can formulate the reactions of the other two thus:

$$(CH_3{\cdot}CO)_2O + 2HNO_3 \longrightarrow 2CH_3{\cdot}CO_2H + NO_2^+ + NO_3^-$$

$$CH_3{\cdot}CO{\cdot}O{\cdot}NO_2 + HNO_3 \longrightarrow CH_3{\cdot}CO_2H + NO_2^+ + NO_3^-$$

Our results do not support Dunning and Nutt's view [2] that acetyl nitrate is effectively nitronium acetate in nitric acid solution. Apart from the unlikelihood of the presence of

the acetate ion in such an acid medium, this interpretation does not account for the presence of dinitrogen pentoxide in the vapour, which shows up directly in the vapour-pressure method.

The minima in the total pressures for the acetic anhydride and acetyl nitrate systems (see Tables 5 and 6) do not seem to have been recorded before (see, *e.g.*, Vandoni and Viala [7]), and the azeotrope in the acetic acid–nitric acid system, which has previously been observed in boiling-point studies,[8] is now clearly reflected in the vapour pressure (Table 4).

Potassium sulphate. In view of the weakness of the hydrogen sulphate ion as an acid in aqueous systems, potassium sulphate should be completely solvolysed into a mixture of the hydrogen sulphate and nitrate:

$$K_2SO_4 + HNO_3 \longrightarrow 2K^+ + HSO_4^- + NO_3^-$$

This explains the observed $\nu = 4$ and also the fact that the solid in equilibrium with the solution after saturation was found by analysis to have the composition of anhydrous potassium hydrogen sulphate. Further additions of potassium sulphate after saturation produced (after equilibration) depressions of the vapour pressure equivalent to those to be expected from potassium nitrate. Some modification to this simple interpretation may be necessary at higher concentrations, since preliminary measurements indicate that potassium hydrogen sulphate dissolved in pure nitric acid yields a vapour containing an excess of dinitrogen pentoxide. Further work is in progress.

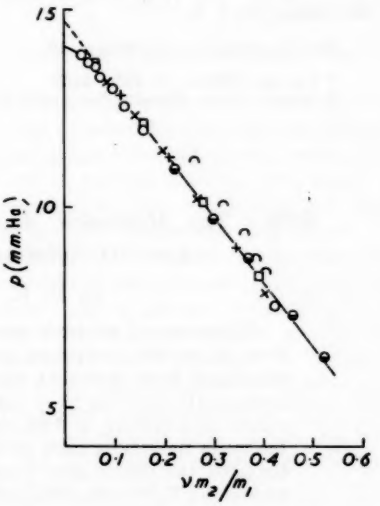

FIG. 2. *The empirical determination of ν values for solutes in nitric acid.*

○, H_2O with $\nu = 1$; ×, KNO_3 with $\nu = 2$; +, NH_4NO_3 with $\nu = 2$; ⊖, KH_2PO_4 with $\nu = 2{\cdot}5$; □, K_2SO_4 with $\nu = 4$; ◠, N_2O_5 with $\nu = 2$.

Sulphuric acid. Our results agree well with Vandoni's [9] in this region of composition. No overall straight line is obtained when the data are plotted as in Figs. 1 and 2, indicating that changes occur in the extent of some reaction as the concentration of sulphuric acid is increased (see, *e.g.*, Fénéant and Chédin [10] for one possibility). Since the nitrate and nitronium ions are supposed to exist together near the composition of pure nitric acid, a shift in the position of the equilibrium

$$NO_3^- + 2H_3O^+ \rightleftharpoons 3H_2O + NO_2^+$$

[7] Vandoni and Viala, *Mém. Services chim. État*, 1945, **32**, 80.
[8] Taylor and Follows, *Canad. J. Chem.*, 1951, **29**, 461.
[9] Vandoni, *Mém. Services chim. État*, 1944, **31**, 87.
[10] Fénéant and Chédin, *Comp. rend.*, 1956, **243**, 41.

must occur in some range of the nitric acid–sulphuric acid system, but it is difficult to reconcile changes of this kind with our present method of determining ν. It is, however, significant that the results for perchloric acid are similar to those for sulphuric acid.

The Self-dissociation of Nitric Acid.—The straight line in Fig. 2 projected back towards the pressure axis reached the vapour pressure of the pure solvent at a value of m_2/m_1 corresponding to the total concentration of dissociation products in the pure acid. From the results for water and potassium nitrate the total mole-fractions of dissociation products at 0°, 10°, and 20° were found to be 0·040, 0·033, and 0·028, respectively, indicating that the extent of dissociation decreases with increasing temperature, as has also been deduced from conductance [11] and thermal data.[12] If the dissociation reaction is represented as $2HNO_3 \rightleftharpoons NO_2^+ + NO_3^- + H_2O$, the mole-fractions of the nitronium ion in the pure acid at the three temperatures become 0·013, 0·011, and 0·009, which are slightly lower than would be expected from the values at other temperatures summarized by Lee and Millen.[11]

We thank the University of Sheffield for the award of a Robert Styring Postgraduate Scholarship to L. L.

THE UNIVERSITY, SHEFFIELD, 10. [*Received, April 18th*, 1957.]

[11] Lee and Millen, *J.*, 1956, 4463.
[12] Wyatt, *Trans. Faraday Soc.*, 1956, **52**, 806.

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859. *The Molecular Association of Some Carboxylic Acids in Aqueous Solution from e.m.f. Measurements.*

By G. R. NASH and C. B. MONK.

The standard electrode potentials of the silver–silver chloride electrode from 15° to 45° in aqueous acetic, propionic, and butyric acids have been calculated from potential measurements obtained with the cell H_2|HCl, aqueous HA|AgCl|Ag (A = carboxylate ion), small concentrations of hydrochloric acid and up to 0·6m-organic acid being used. Similar molalities of the latter have been used in the buffered type of cell whereby Harned has obtained the dissociation constants of weak acids from e.m.f. measurements, *i.e.*, H_2|HA,NaA,NaCl|Ag|AgCl, and by using the known dissociation constants of the acids and the derived standard electrode potentials, the dimerisation constants of these acids have been calculated. The results are of the same order as, but somewhat lower than, those obtained by other methods. There are several unknown factors involved and the effects of these are discussed.

ONE of the most widely used and precise ways of obtaining the dissociation constants of weak acids in solution is by means of the " buffered " e.m.f. cell developed by Harned, *i.e.*,

$$H_2|Pt|HA(m_1), MA(m_2), MX(m_3)|AgX|Ag \qquad \text{(cell I)}$$

where HA is the weak acid, M a metal cation (usually Na^+), X^- a halide (usually Cl^-), A^- is the anion of the acid, and the quantities m are in molalities. This cell was first used by Harned and Ehlers [1] for the study of aqueous acetic acid, and has since been used with many weak electrolytes in a variety of solvents and over wide temperature ranges.[2,3]

[1] Harned and Ehlers, *J. Amer. Chem. Soc.*, 1932, **54**, 1350.
[2] Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, 1943, Ch. 15.
[3] Stokes and Robinson, " Electrolyte Solutions," Butterworths, London, 1955, Ch. 12.

The basic equations to obtain K, the thermodynamic dissociation constant of the acid HA, are

$$E = E_o - k \log m_H m_X f_H f_X \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$K = m_H m_A f_H f_A / m_{HA} f_{HA} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

whence $(E - E_o)/k + \log (m_{HA} m_X / m_A) = - \log K + \log (f_X f_{HA} / f_A) = - \log K' \quad . \quad (3)$

In these $k = 2{\cdot}303RT/F$, f represents ion activity coefficients, E is the measured potential corrected to 1 atm. of hydrogen, and E_0 is the standard electrode potential of the $X^-|AgX|Ag$ electrode.

Since $m_{HA} = m_1 - m_H$, $m_X = m_2$, and $m_A = m_3 + m_H$, K' is easily found by a short series of approximations. Probably the most convenient way of calculating m_H is by means of eqn. (1), using an approximate form of the Debye–Hückel activity-coefficient expression such as that given by Davies,[4] which in a generalised form can be written

$$- \log f_i = A z_i^2 \{ I^{\frac{1}{2}} / (1 + I^{\frac{1}{2}}) - 0{\cdot}2\, I \} = A\, \phi(I) \quad . \quad . \quad . \quad . \quad (4)$$

The factor A depends on T and D (dielectric constant), and the ionic strength I is $I = m_2 + m_3 + m_H$.

On theoretical grounds both f_{HA} and the ratio f_X/f_A should be very close to unity, and some experimental data which confirm this have been collected by Gimblett and Monk.[5] Further confirmation that the ratio $f_{Cl}/f_A = 1$ is given by the following activity coefficients for sodium salts in 0·1m-solution: [6] chloride = 0·778, acetate = 0·791, propionate = 0·800, butyrate = 0·800. Accordingly K', as calculated by eqn. (3), should not vary very much with increasing molalities of one or all of the cell constituents up to about $I = 0{\cdot}1$. In practice, marked variations are found, and three of the possible explanations for these are: (*a*) E_o (at constant T) depends upon the solvent composition, particularly the concentration of HA, so that the values obtained from data for aqueous hydrochloric acid are not applicable, (*b*) a fraction of the organic acid is present as dimers, and (*c*) the dielectric constant of the medium decreases as the molality of HA increases.

The first of these factors has already received some consideration by Harned and Owen [7] in a general survey of E_o values in mixed aqueous organic solvents. They have calculated E_o values at 25° in acetic acid solutions up to 60% of acid. There are very marked changes; thus in water at 25°, E_o for the silver–silver chloride electrode is 0·2224 v, while in 10% acetic acid it is 0·2105 v. Their calculations are based on e.m.f. measurements obtained by Harned and Robinson [8] with the cell $H_2|HA(m_1)$, $NaCl(m_3)$, water$|AgCl|Ag$, which was the first type used by Harned to obtain dissociation constants. In the present work hydrochloric acid has been used in preference to sodium chloride since it suppresses the dissociation of HA, and provides a bigger concentration of H^+ ions. By this means E_o data for acetic, propionic, and *n*-butyric acid solutions up to 0·6m and from 15° to 45° have been obtained. It turns out, however, that if the correct E_o values had been used to calculate K', then the variations with the HA molality would be even more marked.

The second point, namely, that dimerisation occurs, is supported by various experimental approaches which have been summarised elsewhere (some data are given in Table 4). To study this in detail we have obtained data by using Cell I, taking low concentrations of NaA and NaCl, and using high concentrations of HA.

The third point, concerning the dielectric constants of the media, is referred to later.

[4] Davies, *J.*, 1938, 2093.
[5] Gimblett and Monk, *Trans. Faraday Soc.*, 1954, **50**, 1965.
[6] Ref. 3, p. 477.
[7] Ref. 2, Ch. 15.
[8] Harned and Robinson, *J. Amer. Chem. Soc.*, 1928, **50**, 3157.

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TABLE 1. *E_0 Values of the* AgCl|Ag *electrode in acetic, propionic, and* n*-butyric acid solution from* 15° *to* 45° (*cell* II).

Acetic acid.

10^2m_1 = (*a*) 10·00, (*b*) 20·00, (*c*) 40·00, (*d*) 60·00
10^4m_4 = (*a*) 43·70, (*b*) 42·05, (*c*) 48·45, (*d*) 56·31

	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*d*)
		15°				20°		
E (mv).....	498·83	498·25	488·47	479·54	500·60	499·90	489·99	480·89
E_0 (mv)	227·82	227·23	225·78	224·55	224·76	224·17	222·72	221·41
		25°				30°		
E (mv).....	502·21	501·41	491·36	482·10	503·59	502·80	492·57	483·16
E_0 (mv)	221·63	220·97	219·51	218·19	218·29	217·59	216·16	214·77
		35°				40°		
E (mv).....	504·85	504·03	493·71	484·08	505·91	505·16	494·72	484·85
E_0 (mv)	214·77	214·04	212·59	211·17	211·05	210·41	208·96	207·40
		45°						
E (mv).....	506·92	506·19	495·56	485·47				
E_0 (mv)	207·27	206·57	205·09	203·46				

Propionic acid.

10^2m_1 = (*a*) 10·00,* (*b*) 20·00, (*c*) 40·00, (*d*) 60·00
10^4m_4 = (*a*) — , (*b*) 45·83, (*c*) 47·14, (*d*) 50·56

	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*d*)
		15°				20°		
E (mv).....	—	494·79	490·25	484·28	—	496·49	491·74	485·78
E_0 (mv)	227·60 *	226·68	225·44	223·85	224·65 *	223·70	222·29	220·82
		25°				30°		
E (mv).....	—	498·05	393·25	487·10	—	499·37	494·52	488·34
E_0 (mv)	221·45 *	220·56	219·16	217·59	218·10 *	217·18	215·80	214·24
		35°				40°		
E (mv).....	—	500·58	495·64	489·36	—	501·58	496·62	490·34
E_0 (mv)	214·65 *	213·70	212·26	210·70	210·95 *	209·92	208·46	206·95
		45°						
E (mv).....	—	502·52	497·56	491·16				
E_0 (mv)	207·30 *	206·11	204·69	203·12				

n-Butyric acid.

10^2m_1 = (*a*) 20·00,* (*b*) 30·00, (*c*) 40·00, (*d*) 50·00, (*e*) 60·00
10^4m_4 = (*a*) — , (*b*) 28·16, (*c*) 29·10, (*d*) 28·83, (*e*) 18·44

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
			15°					20°		
E (mv).....	—	511·28	507·45	505·79	518·72	—	513·39	509·31	507·59	520·72
E_0 (mv)	226·70 *	225·74	224·83	224·27	223·84	223·70 *	222·78	221·66	221·05	220·55
			25°					30°		
E (mv).....	—	515·24	511·20	509·16	522·71	—	517·00	512·93	510·97	524·64
E_0 (mv)	220·47 *	219·54	218·50	217·58	217·25	217·15 *	216·21	215·16	214·32	213·83
			35°					40°		
E (mv).....	—	518·60	514·54	512·56	526·60	—	520·08	516·07	514·20	528·63
E_0 (mv)	213·65 *	212·64	211·64	210·79	210·37	210·05 *	208·94	208·04	207·30	206·96
			45°							
E (mv).....	—	521·48	517·44	515·49	530·36					
E_0 (mv)	206·20 *	205·13	204·22	203·39	203·19					

* Interpolated from the values in water and the lowest molalities of *m*.

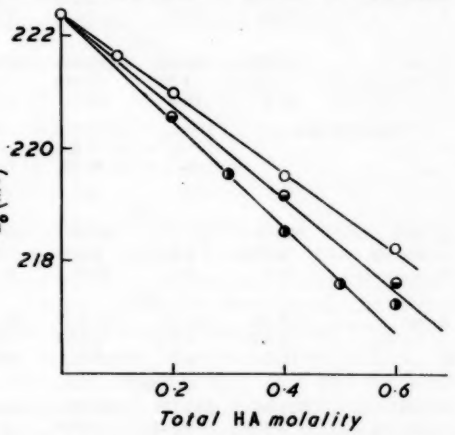
Determination of E_o Values in Aqueous Organic Acids.—For the cell

$$H_2|Pt|HA(m_1),\ HCl(m_4)|AgCl|Ag \qquad \text{(cell II)}$$

from eqns. (1), (2), and (4),

$$\log m' = \log K + 2A\phi(I) + \log (m_1 - m' - 2x) - \log (m_4 + m')$$
$$E_o = E + k \log (m_4 + m')m_4 - 2A\phi(I)$$

where m' is the molality of H^+ ions resulting from the dissociation of the organic acid, x is the concentration of dimers, K is taken as the value in water, and $I = m_4 + m'$. Since x is unknown, it has been ignored in the calculations. The consequences of this are discussed later. The resulting E_o values are given in Table 1. In calculating these, the values of k and A were taken from the tables of Harned and Robinson [9] except that 0·009 was subtracted from A at each temperature (since Davies [4] takes $A = 0{\cdot}500$ at 25° instead of 0·509). The conventional corrections of the measured potentials to 1 atm. of hydrogen



Plot of E_o values at 25° against total HA *molality.*
○ = Acetic, ◒ = propionic, ◑ = *n*-butyric acid.

were based on the vapour pressures of water since the vapour pressures of the solutions are almost identical with these.[10] The K values used are those obtained by Harned and his associates [11] by extrapolating K' data for dilute solutions against I, which, although it is a somewhat empirical procedure, removes errors due to various causes.

The E_o values at any one temperature decrease almost linearly with the molality of HA, the change being most marked with butyric acid. These effects are illustrated by the Figure.

Estimation of the Dimerisation Constants from e.m.f. Data.—By using cell I with molalities of HA ranging from 0·1 to 0·6, and using the E_o values of Table 1, values of m_H were calculated by eqn. (1). To minimise errors resulting from the use of a general type of activity coefficient expression (eqn. 4), and to ensure as much as possible that $f_{Cl}/f_A = 1$, low concentrations of NaA $= m_2$ and of NaCl $= m_3$ were taken. The concentrations of single HA molecules were then calculated from

$$\log m_{HA} = \log m_H m_A - \log K - 2A\phi(I)$$

where $m_A = m_2 + m_H$, and the K values are those obtained by Harned and his associates. Then, the dimers being represented by $(HA)_2$, and the equilibrium constant for the process $(HA)_2 = 2HA$ by L, *i.e.*, $L = (m_{HA})^2/m_{(HA)_2}$, where $m_{(HA)_2} = 0{\cdot}5(m_1 - m_{HA} - m_H)$, the results shown in Table 2 were obtained.

[9] Ref. 3, pp. 456, 491.
[10] "International Critical Tables," McGraw-Hill, New York, 1928, III, pp. 306, 290, 291.
[11] Ref. 2, p. 580.

TABLE 2. *Dimerisation constants of acetic, propionic, and* n*-butyric acids in aqueous solution from e.m.f. data* (15—45° C) (*cell* I).

Acetic acid. 10^2m_1 = (*a*) 10·00, (*b*) 20·00, (*c*) 40·00, (*d*) 60·00
10^4m_2 = (*a*) 72·13, (*b*) 79·07, (*c*) 84·37, (*d*) 100·10
10^4m_3 = (*a*) 82·62, (*b*) 99·05, (*c*) 100·06, (*d*) 116·60

	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*d*)
	15°				20°			
E (mv).....	555·00	535·84	519·95	509·63	557·52	537·93	521·88	511·48
− log m_H ...	3·533	3·280	3·029	2·929	3·531	3·276	3·029	2·928
L	17·3	17·7	17·1	20·6	16·7	21·7	17·2	18·3
	25°				30°			
E (mv).....	560·02	540·25	523·78	513·20	526·45	542·28	525·29	514·85
− log m_H ...	3·529	3·277	3·025	2·927	3·529	3·277	3·027	2·927
L	19·5	15·3	19·8	17·5	17·0	15·5	17·1	17·5
	35°				40°			
E (mv).....	564·90	544·42	527·41	516·53	567·30	546·50	529·20	518·09
− log m_H ...	3·533	3·282	3·030	2·932	3·539	3·286	3·035	2·937
L	18·8	15·0	17·6	17·2	15·6	15·6	18·3	17·0
	45°							
E (mv).....	569·73	548·52	530·88	519·69				
− log m_H ...	3·546	3·292	3·040	2·944				
L	15·6	16·4	19·7	16·3				

Propionic acid. 10^2m_1 = (*a*) 10·00, (*b*) 20·00, (*c*) 40·00, (*d*) 60·00
10^4m_2 = (*a*) 77·69, (*b*) 67·89, (*c*) 69·66, (*d*) 66·51
10^4m_3 = (*a*) 92·18, (*b*) 104·73, (*c*) 89·83, (*d*) 82·63

	(*a*)	(*b*)	(*c*)	(*d*)	(*a*)	(*b*)	(*c*)	(*d*)
	15°				20°			
E (mv).....	560·37	537·17	525·02	516·22	563·15	539·57	527·22	518·30
− log m_H ...	3·674	3·339	3·084	2·924	3·673	3·338	3·086	2·923
L	10·9	9·9	10·9	11·5	10·9	9·7	9·6	11·1
	25°				30°			
E (mv).....	565·78	541·85	529·35	520·34	568·43	544·09	531·35	522·28
− log m_H ...	3·673	3·337	3·084	2·925	3·675	3·340	3·087	2·928
L	10·7	9·8	10·2	10·2	9·7	9·3	8·7	10·1
	35°				40°			
E (mv).....	571·06	546·33	533·37	524·29	573·76	548·50	535·41	526·17
− log m_H ...	3·679	3·344	3·092	2·935	3·688	3·352	3·101	2·942
L	9·9	9·1	9·3	9·1	9·9	9·5	9·1	9·3
	45°							
E (mv).....	576·23	550·74	537·36	528·07				
− log m_H ...	3·695	3·361	3·107	2·951				
L	9·5	8·1	8·9	8·6				

n-Butyric acid. 10^2m_1 = (*a*) 20·00, (*b*) 30·00, (*c*) 40·00, (*d*) 50·00, (*e*) 60·00
10^4m_2 = (*a*) 44·99, (*b*) 48·04, (*c*) 44·18, (*d*) 50·40, (*e*) 87·22
10^4m_3 = (*a*) 47·43, (*b*) 66·57, (*c*) 44·80, (*d*) 58·58, (*e*) 98·92

	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*a*)	(*b*)	(*c*)	(*d*)	(*e*)
			15°					20°		
E (mv)...	545·08	528·73	530·28	521·75	514·62	547·95	531·31	532·94	532·82	516·94
− log m_H	3·158	3·027	2·906	2·876	2·964	3·163	3·031	2·914	2·877	2·973
L	6·5	6·6	8·1	5·9	6·7	6·8	7·0	7·4	6·5	6·3
			25°					30°		
E (mv)...	550·71	533·73	535·49	525·88	519·18	553·43	536·12	537·84	528·33	521·46
− log m_H	3·170	3·037	2·921	2·882	2·980	3·177	3·043	2·926	2·890	2·990
L	6·5	7·1	7·3	6·6	6·1	6·4	7·1	7·6	6·3	5·8
			35°					40°		
E (mv)...	556·11	538·65	540·30	530·49	523·74	558·79	540·91	542·66	532·92	525·80
− log m_H	3·187	3·055	2·936	2·898	2·999	3·198	3·066	2·945	2·909	2·004
L	6·8	6·9	7·7	6·8	6·1	7·0	6·9	8·1	6·7	6·8
			45°							
E (mv)...	561·36	543·15	545·02	535·01	528·38					
− log m_H	3·210	3·076	2·957	2·920	2·023					
L	7·1	7·3	7·9	6·8	6·0					

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Discussion

As Table 3 shows, there are no marked changes in L with temperature. This agrees with the conclusions of Davies and Griffiths,[12,13] who used freezing-point and distribution methods for studying dimerisation in aqueous acetic and butyric acids, and also with Trayhard's [14] observations which were based on Raman spectra studies of aqueous acetic acid.

Table 3. *Average L values from the e.m.f. data.*

Temp.	15°	20°	25°	30°	35°	40°	45°
Acetic acid ...	18·2 ± 1·2	18·5 ± 1·6	18·0 ± 1·6	16·8 ± 0·6	17·2 ± 1·1	16·6 ± 1·0	17·0 ± 1·4
Propionic acid	10·8 ± 0·5	10·3 ± 0·7	10·2 ± 0·2	9·5 ± 0·6	9·5 ± 0·4	9·5 ± 0·3	8·8 ± 0·5
n-Butyric acid	6·8 ± 0·6	6·8 ± 0·3	6·7 ± 0·4	6·6 ± 0·6	6·9 ± 0·4	7·1 ± 0·4	7·0 ± 0·5

A comparison of the dimerisation constants obtained by various methods (Table 4) reveals that the e.m.f. values, although of the same order as those obtained in other ways, are somewhat the smaller. The tendency to dimerise increases as the chain length grows. (The value for propionic acid by conductance–viscosity is not very reliable, being the mean of 22, 22·5, and 15, calculated from measurements with very dilute solutions.)

Table 4. *Values of L obtained by various methods.*

	Acetic acid	Propionic acid	*n*-Butyric acid
Freezing point [12,13] (0°)	28	—	11
F.p.–distribution [12,13] (25°)	28	—	10
Vapour pressure [12] (25°)	20 ± 3	—	—
Conductance–viscosity [15] (25°)	19 ± 2	20 ± 3	11 ± 0·6
E.m.f. (25°)	18 ± 1·6	10·2 ± 0·2	6·7 ± 0·4

There are several reasons which could account for the fact that the L values from the e.m.f. data are smaller than those obtained in other ways, and originate from the factors referred to earlier. Among these is one about which no precise information is available, namely, the dielectric constants (D) of the solutions. However, there is sufficient evidence to indicate that the presence of organic acids lowers the dielectric constant from that of water, since $D = 6·2$ and 2·9 for pure acetic acid [16] and butyric acid,[17] respectively, and Drude,[18] who studied concentrated propionic acid, reported that $D = 43·8$ for a 55% solution at 17° (D for water is 81·5). These figures suggest that the dielectric constants of the 0·6m-solutions are about three units lower than that of water at the corresponding temperature. This would influence both the value of K and the Debye–Hückel factor A in eqn. (4). Nevertheless, even if the dielectric constants were known exactly, as Stokes and Robinson have pointed out,[3] it is not possible to calculate the precise extent to which the values of K are altered from those in water. Born's equation,[19] which should predict this change, proves under test to be only an approximation. With mixed solvents such as alcohol–water and dioxan–water marked specific effects are found which no doubt are the result of ion–solvent interactions. Calculation shows that even the average change of log K with $1/D$ from known data for alcohols–water and dioxan–water [3] is excessive, since, if this is used together with the estimate that D changes by 3 units from water to 0·6m-acetic acid, the calculated molality of undissociated single molecules becomes greater than 0·6. However, on taking, *e.g.*, the results at 25°, if K (acetic acid) changes from $1·745 \times 10^{-5}$ in water [11] to $1·68 \times 10^{-5}$ in 0·6m-acid, L is raised from 18 to 28, and similarly if K (butyric acid) [11] changes from $1·515 \times 10^{-5}$ to $1·37 \times 10^{-5}$, L is raised from 6·7 to 11. (For both of these estimates it is assumed that D changes by 3 units, *i.e.*, the Debye factor A is raised from 0·50 to 0·55.) At the same time, the standard electrode potentials change

[12] Davies and Griffiths, *Z. phys. Chem.* (*Frankfurt*), 1954, **2**, 353.
[13] *Idem*, *ibid.*, 1956, **6**, 143.
[14] Trayhard, *Compt. rend.*, 1945, **223**, 202.
[15] Cartwright and Monk, *J.*, 1955, 2500.
[16] Le Fèvre, *Trans. Faraday Soc.*, 1938, **34**, 1127.
[17] Ref. 10, VI, 87.
[18] Drude, *Z. phys. Chem.*, 1897, **23**, 267.
[19] Born, *Z. Physik*, 1920, **1**, 45.

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slightly from those given in Table 1. The two concerned here for example become 0·6 mv and 1·1 mv lower, respectively.

Finally, since the existence of dimers was ignored in calculating the E_0 values of Table 1, it has been implied that the dissociation constants of equilibria such as $(HA)_2 = H^+ + HA_2^-$ are twice as large as those of the single molecules. If the dimers do not dissociate, then both the E_0 and L values are different from those given in the Tables or when the effect of changing dielectric constant is considered. For instance, with 0·6m-acetic acid at 25°, if we take the lower K of $1{\cdot}68 \times 10^{-5}$ suggested in the previous paragraph, and the higher Debye factor of 0·55, and also assume that the dimers do not dissociate, E_0 becomes 0·8 mv lower than the value given in Table 1, and L becomes 25, compared with the original estimate of 18 in Table 2, and the higher result of 28 when the dielectric constant effect and not the dimer dissociation is considered.

The general conclusion, therefore, is that the present interpretation of potential measurements can give some measure of the dimerisation process but the precision of the answers is markedly lowered by several unknown features.

Experimental

The conventional H-shaped cell was used for the e.m.f. measurements. It contained a tap with a wide bore in the tube connecting two electrode compartments, which was only opened when readings were being taken. The gas exits consisted of U-shaped capillary tubes, and the electrodes were fitted into the cell by means of standard ground-glass joints. The measuring apparatus consisted of a Tinsley potentiometer (type 4025), Tinsley Weston cells (type 1267), and Pye "Scalamp" galvanometer (No. 7904/5) with a sensitivity of 7·24 μv/mm. The potentiometer could be read to 0·1 mv, and the nearest 0·01 mv could be estimated from the galvanometer.

The cell and gas saturators were fixed in a water thermostat kept at the required temperatures to within ±0·03°, and the saturators were filled with the solution being studied to prevent concentration changes in the cell. Commercial B.O.C. nitrogen and hydrogen (purified by passage over palladium–abestos pellets) were passed through the silver–silver chloride and platinum-black electrode compartments, respectively, overnight before starting a "run." Several types of silver–silver chloride electrode were tried before final choice of the thermal-electrolytic type of Noyes and Ellis,[20] and Lewis.[21] The electrolytic type described by Brown [22] would not maintain a constant potential in the concentrated carboxylic acid solutions. The electrodes used remained constant during a "run" to within 0·05 mv, but to minimise errors due to the slight lack of reproducibility an electrode was used for a series of E_0 determinations in a particular HA molality, and then used for L determinations at the same HA molality. A fresh electrode was used for each such set of measurements.

"AnalaR" acetic acid, sodium hydroxide, sodium chloride, and hydrochloric acid were used. Stock solutions were prepared with conductivity water obtained by passing distilled water through a mixed-bed ion-exchange column. The propionic and *n*-butyric acids were purified by fractionation, the fractions of b. p. 140—140·7°/735 mm. and 163·0°, respectively, being collected. Solutions of the carboxylic acids were standardised by carbonate-free sodium hydroxide which was standardised by potassium hydrogen phthalate. The chloride stock solutions were standardised gravimetrically *via* silver chloride. The cell solutions were made up on a molality basis, *viz.*, per 1000 g. of water + carboxylic acid, by analogy with the conventional procedure with mixed solvents.

Thanks are expressed to the Department of Scientific and Industrial Research for a maintenance grant (to G. R. N.), and to Dr. D. J. G. Ives (Birkbeck College, University of London) for his guidance in choosing suitable measuring instruments. The potentiometer and a calculating machine were made available by the Government Grants Committee of the Royal Society.

The Edward Davies Chemical Laboratories,
University College of Wales, Aberystwyth. [*Received, May 7th,* 1957

[20] Noyes and Ellis, *J. Amer. Chem. Soc.*, 1917, **39**, 2532.
[21] Lewis, *ibid.*, 1906, **28**, 166.
[22] Brown, *ibid.*, 1934, **56**, 646.

860. *The Decomposition of Barium Styphnate Trihydrate.*

By F. C. Tompkins and D. A. Young.

The kinetics of the decomposition of the anhydride of barium styphnate trihydrate have been investigated. The marked differences found between the behaviour of this anhydride and that derived from the monohydrate show that the kinetics and, to a less extent, the activation energy are dependent on the topography of the reactant matrix.

As far as the authors are aware, the thermal stability of barium styphnate trihydrate, particularly in relation to the monohydrate, has not as yet been investigated. We report here a kinetic study of the isothermal decomposition of the trihydrate and compare the results with those obtained in our investigation of the dehydration and decomposition of the monohydrate,[1] where references to experimental techniques can be found.

The gamboge-coloured trihydrate is much easier to dehydrate than the monohydrate; the latter dehydrates slowly above 110° *in vacuo* with an activation energy of 26 kcal./mole,

Fig. 1. *Typical plots of pressure against time. The lowest curve refers to an "interrupted" run.*

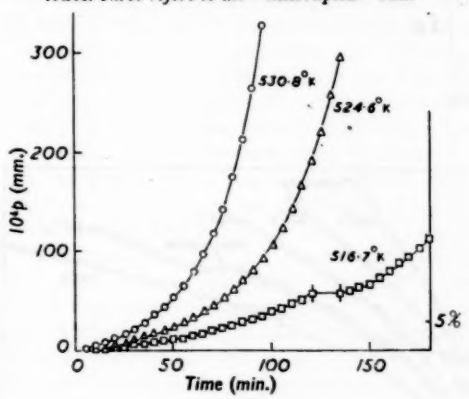
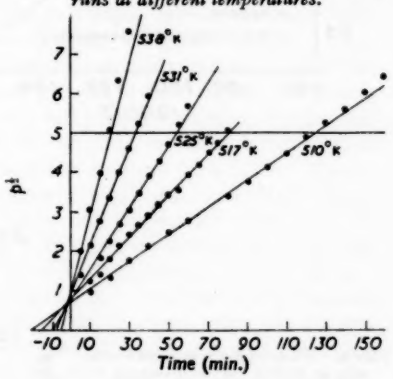


Fig. 2. *Plots of* p½ *against* t *for a series of runs at different temperatures.*



whereas the trihydrate loses all its water of crystallisation *in vacuo* in 20 min. at room temperature. On subsequent exposure to air, the reddish-brown anhydride so formed takes up one molecule of water to form a stable monohydrate which is indistinguishable by *X*-ray analysis from that obtained from solution. Similarly, the dehydration and decomposition characteristics are identical with those previously reported for the "normal" monohydrate. It may be noted that trihydrate stored under normal conditions in laboratory air slowly changes over a two-year period to a bright lemon-yellow indicating superficial conversion into the monohydrate on storage.

The main interest here was whether the anhydride formed by rapid low-temperature dehydration of the trihydrate would decompose thermally in the same way as the anhydride formed by the higher-temperature dehydration of the monohydrate, it having previously been shown[1] that dehydration of the monohydrate is complete at its decomposition temperature. Decomposition of the "trihydrate anhydride" proceeds smoothly between 236° and 265° and above 265° explosion normally occurred, whereas the temperature range for the smooth decomposition of the "monohydrate anhydride" is higher, *viz.*,

[1] Young and Tompkins, *Trans. Faraday Soc.*, 1956, **52**, 1245.

269—308°, and explosions occur for whole crystals above 300° after about 45% decomposition. Similarly, marked differences are found in the kinetics of decomposition of the two forms.

Typical pressure against time plots for the decomposition of the " trihydrate anhydride," including an interrupted run, are given in Fig. 1. We have plotted these in Fig. 2 according to the equation

$$p^{\frac{1}{3}} = k(t + t_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

found valid in the previous investigation. Straight lines with negative time intercepts are obtained up to 5% decomposition only, with large positive deviations above, the intercept

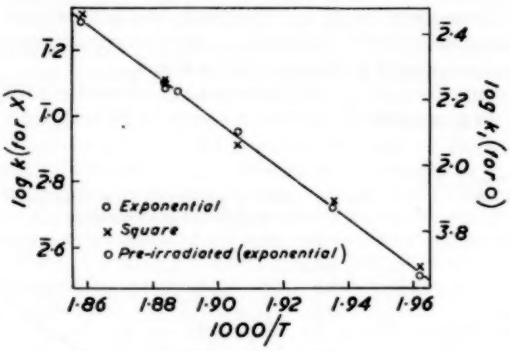


FIG. 3. *Arrhenius plots*: log k *from eqn.* (1) (*left-hand ordinate*) *and* log k_1 *from eqn.* (2) (*right-hand ordinate*) *against* 1/T (° K) *to give* E = 33·5 *kcal./mole.*

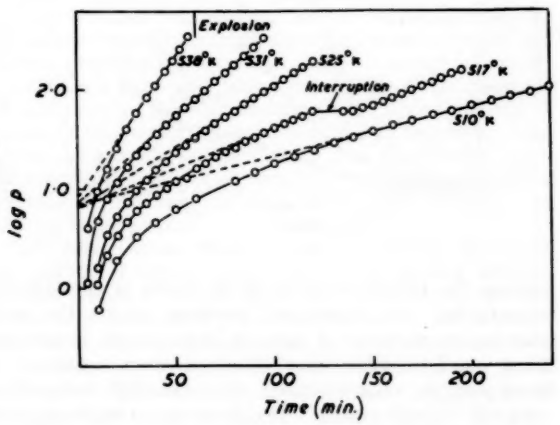


FIG. 4. *Plots of* log p *against* t—*the run at* 517° K *was interrupted.*

t_0 being temperature-dependent; however, for the " monohydrate anhydride," the equation was valid from 10 to 45% decomposition and t_0 was independent of temperature. The activation energy, derived from the temperature coefficient of k and also from that of $(1/t_0)$, is 33·5 ± 0·8 kcal./mole (see Fig. 3) compared with a corresponding value of 36·5 ± 0·6 kcal./mole for the monohydrate anhydride.

Above 5% decomposition, the plot of the logarithm of the pressure of gas evolved against time is a straight line but below 5% there are negative deviations from this line (Fig. 4), and the intercept at zero time is independent of temperature. The expression

$$p = C \exp(k_1 t) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C is a constant independent of temperature and k_1 is a rate constant, holds up to the inflexion point at about 45% decomposition. The activation energy derived from the temperature coefficient of k_1 is again 33·5 kcal./mole.

The characteristics of the thermal decomposition were unaffected by changes in the temperature of dehydration of the trihydrate or by annealing the anhydride at 120° *in vacuo*. (Annealing in the laboratory atmosphere converted the sample into the monohydrate.) Interruption of a run likewise had no effect on the rate. Although prolonged photolysis with light of λ 2537 Å caused some decomposition, pre-irradiation did not alter the rate of subsequent thermal decomposition.

These results make it evident that the anhydrous matrices obtained by the dehydration of the monohydrate and the trihydrate are physically different, that formed from the trihydrate being less stable as exemplified by the lower activation energy and lower temperature range for measurable rates of decomposition. The topochemical features which determine the rate law are apparently unchanged at 120° provided water vapour is absent; in presence of water vapour conversion into the monohydrate is easy even when the " trihydrate anhydride " had previously been heated to just below its decomposition temperature. Water clearly catalyses the conversion into the monohydrate lattice which is not produced directly from the trihydrate lattice, at least under the conditions used by us. Evidently the activation energy for rearrangement to give the monohydrate is greater than the activation energy for dehydration. Furthermore it is clear from the rapid loss of water from the crystal bulk and the relatively rapid take-up of water with formation of the monohydrate that the " trihydrate anhydride " is quite " porous." For the initial 5% decomposition there seems little reason to change the mechanism given for the decomposition of the anhydride of the monohydrate and of that of lead styphnate monohydrate.[2] The dehydrated small crystals of the trihydrate consist of blocks, the faces of which were the sub-grain boundaries of the original crystals; remnants of crystalline structure in a strained metastable condition persist within each block. Nucleation of the sub-grains occurs at the lines of intersection of the sub-grain boundaries where the decomposing unit is least co-ordinated with the lattice and progression of the reaction into the grains proceeds to a small depth up to ~5% decomposition. During this period, eqn. (1) is applicable. With the more stable " monohydrate anhydride " however, this process continues up to 50% decomposition, but with the highly strained lattice of the trihydrate, cracks are propagated through the reactant after 5% decomposition in the manner envisaged by Prout and Tompkins,[3] thereby giving a branching mechanism which leads to the exponential expression given in eqn. (2). The smaller activation energy for decomposition of " trihydrate anhydride " is a consequence of the strain energy at the surfaces of the metastable phase. These investigations on *chemically* identical anhydrides emphasise how the topography of the reactant matrix largely determines the kinetics of the decomposition.

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[2] Young and Tompkins, *J.*, 1956, **3331**.
[3] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.

861. *Crystal Symmetry and the Adsorption of Dyes by Growing Crystals. Part II.* Potassium Nitrate.*

By JOHN WHETSTONE.

The suitability, for adsorption of dyes, of the principal low-index planes of potassium nitrate is discussed in the light of the scheme proposed previously by the author to explain modifications of crystal habit by dyes. Owing to the pseudohexagonal symmetry of the crystals about the axis normal to {001}, it is to be expected that dye adsorption will influence not only formation of pleochroic dye inclusions but also twinning tendencies. Evidence obtained by the study of modified crystals is consistent with the expectations.

THE ordinary-temperature modification of potassium nitrate crystallises in the orthorhombic system. In addition to single crystals, in which {110} and {010} are the only faces normally developed of the zone perpendicular to the basal plane {001}, pseudohexagonal "triplets" twinned on {110} can also crystallise. The earliest reference to the modification of crystal habit by dyes of potassium nitrate is by Retgers.[1] Instead of the usual long prisms, he obtained rounded tablets on {001} in the presence of soluble Nigrosine. This extension of the basal plane {001} has been confirmed to be the characteristic manifestation of "advanced" habit change of this salt with dyes. The crystals obtained may or may not contain pleochroic dye inclusions. They may be well-formed hexagonal {001} tablets, or aggregates of hexagons growing out from one another, lamellæ of very thin platy crystals with characteristic hexagonal outgrowths at the edges, platy crystals showing repeated pseudohexagonal twinning, or lath-like crystals showing occasional twinning rendered visible to the naked eye by virtue of closely crowded parallel striations which run lengthwise along the untwinned portions. The habit modification is very easily recognised by the centred "acute bisectrix" interference figures given by the crystals.

Other modifications of potassium nitrate are sometimes observed. For instance, occasionally platy or lath-like {010} crystals are produced, presumably by dye adsorption on forms of which *b* is the zone axis. Extremely acicular crystals are rarely encountered.

Examination of the Structure of Potassium Nitrate Crystals.—The *X*-ray structural determination employed in this study is that by Edwards.[2] The basal plane {001}, the plane usually developed in area by potent habit-modifiers, is structurally of low reticular density and consists of alternate layers of anions and cations separated by 1·05 Å. The nitrate ions are all coplanar and lying in {001}; so that for reasons given before,[3] the plane does not lend itself well to adsorption of planar sulphonated-dye molecules.

The principal planes perpendicular to {001} fall into two groups, the members of which are related by the pseudohexagonal symmetry of the crystal; {100} and {130} form one group. These forms are of high reticular density, and are composed of alternate rows of anions and cations (see Fig. 1). In {100} the rows are all coplanar, but in {130} the individual rows of anions are not exactly coplanar, two separate layers being formed about 1·07 Å apart. In many cases {100} and {130} may be expected to be equally suitable for dye adsorption; these forms would appear to be especially well adapted to the adsorption of planar dye molecules containing roughly equivalent numbers of anionic and cationic polar substituent groups.

{010} and {110} are the second group. The forms again are of high reticular density but are composed entirely of one kind of ion, planes of anions alternating with planes of cations in the crystal structure. In {010} the constituent ions of the plane are all coplanar

* Part I, *J.*, 1956, 4841.

[1] Retgers, *Z. phys. Chem.*, 1893, **12**, 582.
[2] Edwards, *Z. Krist.*, 1941, **80**, 154.
[3] Whetstone, *Trans. Faraday Soc.*, 1955, **51**, 973, 1142.

FIG. 1. *Fast-red E on potassium nitrate* {100}. *Single circles are* K *ions;* NO_3 *ions are in the plane perpendicular to the paper and are represented edgeways, the two* O *atoms and the* N *atom being shown.*

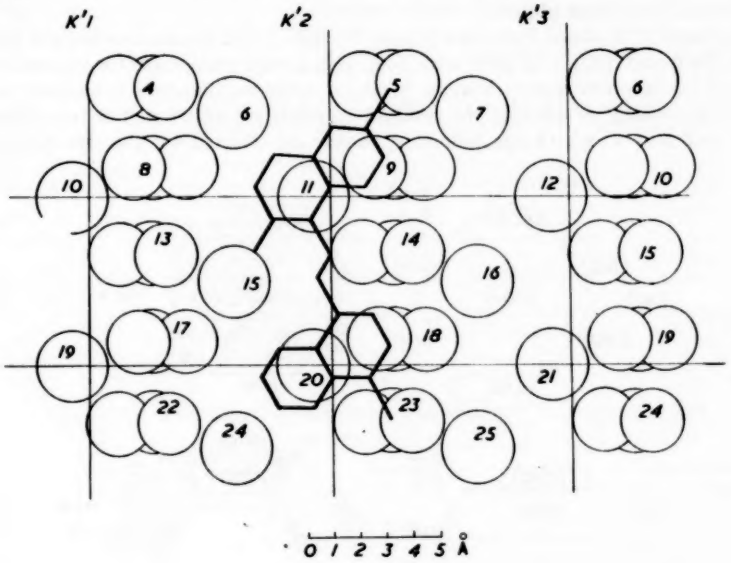
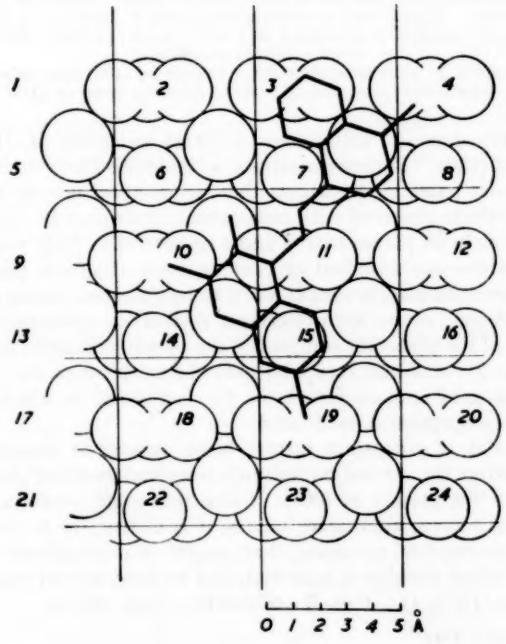


FIG. 2. *Amaranth on potassium nitrate* {010}. *Representation is as in Fig.* 1.



(Fig. 2) but again in {110} the alternate rows of anions lie in two layers separated by about 1·07 Å. In many cases both forms are likely to be equally suited to dye adsorption. The adsorption of dyes with a preponderance of one kind of polar substituent group is likely to be favoured on these planes.

Pleochroism of Modified Potassium Nitrate Crystals.—The similarities and the differences between {010} and {110}, and {100} and {130}, give a very wide scope for various modes of adsorption of different dyes. Various types of habit-modification behaviour are to be expected, depending on whether the resultant crystals are untwinned or pseudohexagonal triplets, and also which of the following planes are selected by the dye molecules for

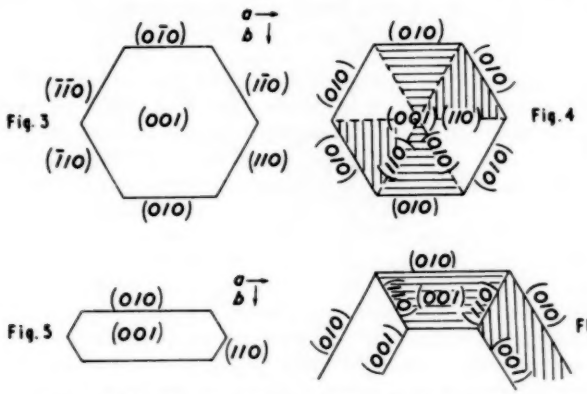


FIG. 3. *Single crystal modified by adsorption on* {010}. *Growth on* {100} *and* {001} *most retarded. Crystal tends to be compact.*

FIG. 4. *Pseudohexagonal triplet modified by adsorption on* {010}. *Growth on* {100} *and* {001} *most retarded. Crystal tends to be hexagonal, owing to twinning on* {110}.

FIG. 5. *Simple crystal modified by adsorption on* {100}. *Growth on* {001} *and* {010} *most retarded. Crystal tends to be lath-like.*

FIG. 6. *Triplet modified by adsorption on* {100}. *Growth on* {100} *least retarded. Triplet shows characteristic elongation of sections, twinning being on* {110}.

adsorption: (*a*) {010} alone, (*b*) {110} alone, (*c*) {110} and {010}, (*d*) {100} alone, (*e*) {130} alone, (*f*) {100} and {130}. Potassium nitrate is therefore likely to follow a more complicated pattern in its habit modifications than ammonium nitrate IV.[4] It is probable that some unusual effects observed with potassium nitrate may be due to the dye's being adsorbed simultaneously on planes with *b* and *c* respectively, their zone axes.

If the dye molecules are adsorbed at once on more than one pinacoid of a pseudohexagonal crystal form, no pleochroism is likely to be observed, owing to the simultaneous interaction of the electric vector with electronic systems in different orientations. However, the structures of the pinacoids comprising the pseudohexagonal forms are not exactly similar, so that if the dye molecule is capable only of adsorption on one component pinacoid the modified crystals may contain pleochroic dye inclusions, in which case the detection of the plane of dye adsorption is facilitated.

The ordinary habit of potassium nitrate being somewhat elongated on {001}, it is apparent that to convert the normal crystals into the usual modified plates a great restraint must be imposed on the growth of {001}. Since this could conceivably be imposed by adsorption of dye on several alternative planes, it is instructive to predict the effects on crystal habit and pleochroism, assuming that growth is most affected on planes perpendicular to those on which the dye is adsorbed, and to compare experimental observations with the predictions (Table 1). Figs. 3—6 illustrate these effects.

[4] Whetstone, *J.*, 1956, 4841.

XUM

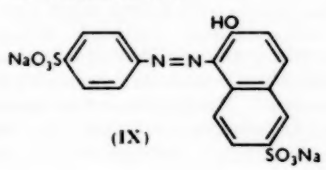
TABLE 1. *The effects of dye adsorptions on various planes on the nature of* {001} *modified crystals of potassium nitrate.*

Plane(s) of adsorption of dye	Predicted effects on modified crystals	
	Single crystals	Triplets
{010} only	Should retard {100} and {001}. Strong pleochroism	Production encouraged owing to restriction of growth on *a*. Pleochroism in units of twins
{100} only	Should retard {010} and {001}. Strong pleochroism	The elongation on *a* should tend to suppress the formation of hexagonal triplets
{110} only	Pleochroism unlikely	No pleochroism
{010} and {110}	Flat hexagonal {001} plates. No pleochroism	No pleochroism
{130} only	Pleochroism unlikely	No pleochroism
{100} and {130}	Flat hexagonal {001} plates. No pleochroism	No pleochroism
Any other planes steeply inclined to {001}	No pleochroism, if planes multiplied by symmetry	No pleochroism
{001}	Pleochroism with unsymmetrical dye molecules only	Pleochroism with unsymmetrical dye molecules only

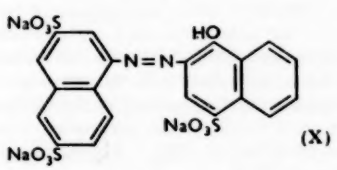
TABLE 2. *Potassium nitrate* {001} *modification: some crystal-habit modifying dyes.*

Structure *	Dye	Plane of adsorption (pleochroism)	Plane of adsorption (fitting)	Location of polar groups on diagram of plane (S = SO_3^- group)
I*d*	Fast-red E	{100}	{100}	S(4′)-23 OH(2)-15, S(6)-5
IX	—	{100}	{100}	S(4′)-23 OH(2)-15, S(6)-5
I*a*	Amaranth	{010}	{010}	S(4′)-4, S(3)-10, S(6)-19
I*b*	D.I.F.	—	{010}	S(4′)-4, S(3)-10, S(6)-19
I*e*	—	—	{010}	S(3′)-10, S(6′)-19, S(4)-4
X	—	—	{100}	OH-11, S(3′)-8, S(6′)-22 (near) S(4)-18
XI	Solochrome-yellow YS	—	{010}	S(6′)-22, S(8′)-14, CO_2H-7
VII*b*	Disulphonated Döbner's violet	—	{100}	$(NH_2)p$-2, $(NH_2)p'$-16, (S)*m*-5, (S)*m*′-18
XII	Ink-blue	—	{010}	S(*p*)-5, S(*p*′)-4, S(*p*″)-23
VIII	1 : 4-Diaminoanthraquinone-2-sulphonate	{100}	{100}	NH_2(1)-6, NH_2(4)-15, S-8
VIII*a*	Acid alizarin-blue	{010}	{010}	S(6)-15, S(2)-2

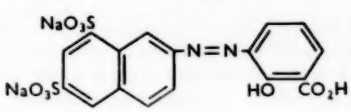
* Formula numbers are those of the earlier Part of the series (ref. 4), with the addition of [I*d*-2-OH, 6 : 4-$(SO_3Na)_2$], [I*e*; 2-OH, 4 : 3′ : 6′-$(SO_3Na)_3$], [VIII*a*; 1 : 3 : 4 : 5 : 7 : 8-$(OH)_6$, 2 : 6; $(SO_3Na)_2$], (IX)—(XI) as annexed, and [(XII), tris-(*p*-sulphonated *N*-phenyl)pararosaniline (VI; R_2 = H, $C_6H_4{\cdot}SO_3Na$-*p*)].



(IX)



(X)



(XI)

The observed pleochroic properties and habit of the modified crystals are usually consistent with the predictions in Table 1, and changes of habit may satisfactorily be explained by similarities between the orientations of polar groups of the dye molecules and the ionic structures of suitable crystal planes.

Experimental

Fast-red (AA) and Amaranth (BA), etc.—Fast-red E and amaranth differ in that the latter has an extra 3-sulphonate group. Whereas amaranth is generally quite a useful crystal-habit modifier, the activity of fast-red E is apparently specific to potassium nitrate. In spite of higher sulphonation, the habit-modifying power of amaranth, with apparently quite adequate solubility, is less than that of fast-red E and not quite the same in character. The habit of the crystals obtained with fast-red E was platy on {001}, and the crystals were much twinned, though rarely to produce complete hexagons, the usual tendency being to produce somewhat elongated crystals joining up at the twinning plane at an angle of 60° with other similar units. The crystals were striated parallel with the lengths of the units, and the dye inclusions in the crystals were markedly dichroic, as predicted in Table 1 for the effect of dye adsorption on {100} of potassium nitrate.

Potassium nitrate has the small optic axial angle of 6°, but in spite of this it was possible to locate the optic axial plane (100) as perpendicular to the elongation and striations of the modified crystals. This indicated that the elongation and striation of the crystals were parallel with their *a* axis, and that twinning was on {110}. The colour of the dye inclusion was at a maximum when the electric vector was parallel to the optic axial plane, so that, if it is assumed that the dye molecules are located in a plane perpendicular to the modified plane, containing the flat nitrate ions, then the dye molecules must be adsorbed on {100}. In agreement with these deductions, it was possible to demonstrate the fitting of fast-red E on to {100}: both sulphonate groups fell into nitrate ion sites, and the hydroxy-group fitted within the radius of an ammonium ion (Fig. 1).

Amaranth in very high concentrations brought about the crystallisation of potassium nitrate as aggregates of small {001} hexagonal platy crystals, apparently pseudohexagonal triplets, not single crystals. Although often strongly coloured, the crystals did not show pleochroism save in a few isolated examples when small patches of colour showed dichroism probably indicating that the amaranth was adsorbed on {010}.

Amaranth does not fit on to {100} with all three sulphonate groups; a better fit is observed on {010} in which all sulphonate groups may be located in anionic sites (Fig. 2).

Sodium 1 : 4-*Diamino-* *and* 1 : 4 : 5 : 8-*Tetra-amino-anthraquinone-2-sulphonate.*—The diamino-compound produced exactly the same habit modification and pleochroism as fast-red E and by similar arguments it was shown to be adsorbed on {100}. The tetra-amino-derivative gave an even more platy habit; the {001} crystals were, however, coloured steel-blue and showed no striations or pleochroism to aid identification.

The diamino-compound fits well into {100}, the two amino-groups and the sulphonate group falling accurately into ionic sites. The tetra-amino-compound, however, will fit neither {100} nor {010}, but it fits excellently (032) with its four amino-groups replacing potassium ions. This plane is repeated owing to the pseudohexagonal symmetry about the *c* axis, which is an adequate explanation of the absence of pleochroism in the modified crystals.

Acid Alizarin-blue (C.I. 1063).—This dye in saturated solution in cold potassium nitrate solution influenced the crystallisation of the salt so that thin extended {100} plates with a matt surface to the naked eye, and with pleochroic dye inclusions, were produced. When microscopically examined under low power between crossed Nicols, the matt surface was found to be due to repeated twinning in the crystals. Parallel striations crossed each separate portion of the composite crystal, parallel to the {100} optic axial plane. The electric vector perpendicular to these striæ produced the maximum colour, so that the inference was that the dye molecules must be adsorbed on {010}. The sulphonate groups can be very accurately located on nitrate ionic sites in {010}.

Acid Magenta and Related Dyes.—Potassium nitrate underwent fairly strong modification of crystal habit on {001} with trisulphonated pararosaniline, but acid-magenta ND, similar, save for the addition of three *meta*-methyl groups to the molecule, had to be used in saturated solution to produce much effect. Trisulphonated Döbner's violet did not appear capable of

modifying potassium nitrate in very significant degree. The *mm'*-disulphonated Döbner's violet, however, showed a habit-modifying power similar in strength to that of trisulphonated pararosaniline.

Definite conclusions were not drawn as to the likely mode of adsorption of these dyes, which gave strongly coloured non-pleochroic crystals.

On balance it appears that the {001} basal plane is most suited to the adsorption of acid-magenta. This is consistent with the absence of pleochroism in the modified crystals since the dye molecules adsorbed on {001} would show trigonal symmetry.

Trypan-red (Benzidine-3-sulphonate ⟶ 2 moles of amino-R-salt).—A very striking agreement observed when the 5-sulphonate groups of the trypan-red molecule were placed on the nitrate ions of {010} drawn to scale led to a prediction of strong modifying power for this dye. This was confirmed by the strong modification of habit to weakly coloured, apparently non-pleochroic {001} leaflets brought about by addition of trypan-red to a slowly crystallising solution of potassium nitrate.

It is possibly noteworthy that a quite good agreement with the pattern of nitrate ions in {100} is also shown by trypan-red, which may explain the lack of pleochroism, if any could be expected in the weakly coloured crystals.

It has not been possible to examine in detail some of the more interesting habit modifications of potassium nitrate owing to ignorance of the probable structures of the dyes concerned, *e.g.*, induline 2B.

Diagrammatical Illustrations of Adsorbed Dyes on Crystal Planes.—Diagrams of the two pinacoids {010} and {100} are reproduced (Figs. 1 and 2) and the dyes amaranth and fast-red E respectively are shown superimposed on the planes. In order to facilitate comparisons of dye structure drawn in accord with the available information with these planes, the ions are all numbered, and the ionic positions on which the polar groups of other dyes considered may be superimposed are given in Table 2. The sulphonate groups of the dyes are depicted merely as carbon–sulphur bonds; it will be understood that the planes of the oxygen triangles of the sulphonate groups are perpendicular to the plane of the dye molecules.

With respect to this and the following paper the author acknowledges the aid of Imperial Chemical Industries Limited, Dyestuffs Division, and Dr. E. K. Pierpoint, who prepared many dyes not listed in the Colour Index, and Professor W. Bradley, Dr. C. H. Giles, and Professor Wilson Baker, who gave many samples of obsolete commercial dyestuffs for testing.

IMPERIAL CHEMICAL INDUSTRIES LIMITED,
RESEARCH DEPARTMENT, NOBEL DIVISION,
STEVENSTON, AYRSHIRE.

[*Received, February 13th*, 1957.]

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862. *Crystal Symmetry and the Adsorption of Dyes by Growing Crystals. Part III.* Sodium Nitrate and Ammonium Sulphate.*

By JOHN WHETSTONE.

The modifications of crystal habit produced in sodium nitrate and ammonium sulphate by dyes are described. The lack of pleochroic dye inclusions observed in the modified crystals is explicable by their respective trigonal and pseudohexagonal symmetry, with dye adsorptions on planes perpendicular or steeply inclined to their modified basal planes.

THE characteristics of a number of modified crystals of sodium nitrate and ammonium sulphate have been examined in the light of previous conclusions as to the effect of dye adsorptions on crystal habit.[1] They are considered together, because pleochroism is not normally encountered in the modified crystals.

The crystal structure of sodium nitrate departs radically from those of ammonium nitrate IV and the ordinary-temperature modification of potassium nitrate. The pseudo-hexagonal character of orthorhombic potassium nitrate, and the arrangement of its ions in

* Part II, preceding paper.

[1] Whetstone, *Trans. Faraday Soc.*, 1955, **51**, 973, 1142.

several layers in the unit cell parallel with the basal plane {001}, are, to a large extent, reproduced in sodium nitrate. The symmetry, however, has become rhombohedral, and the habit of sodium nitrate crystals has changed from the acicular and prismatic forms commonly shown by ammonium and potassium nitrates, to compact rhombs.

Ammonium sulphate is a member of a group of isomorphous salts including chromates and sulphates, all belonging to the orthorhombic system (space group V_h^{16}). The crystal-habit modifications of potassium sulphate and potassium chromate were investigated by Buckley,[2] who, however, predicted that ammonium sulphate would not be a suitable subject for investigation of its habit changes, compared with the above two substances, on account of its higher solubility and consequently its greater " salting out " powers, and also because the {010} plane, which in potassium chromate and sulphate was the one he had found to be enhanced by dyes, was already the predominant plane in the unmodified ammonium sulphate crystal. However, in this present work ammonium sulphate often was found to undergo habit modification with dyes on {001} instead of {010}, although the latter is in fact a frequent crystal-habit change with all salts examined of this group.

Modifications of Crystal Habit of Sodium Nitrate.—Sodium nitrate on crystallising at room temperature was strongly habit-modified to {0001} hexagonal plates by a few dyes, notably trisulphonated pararosaniline or acid-magenta, the acid-greens (Colour Index Nos. 669 and 670), ink-blue (C.I. No. 706), sulphonated Döbner's violet, induline, sodium 1 : 4 : 5 : 8-tetra-aminoanthraquinone-2-sulphonate, and a few bisazo-dyes of the naphthol-black B and Biebrich patent-black BO types (C.I. Nos. 315 and 320, respectively). Other dyes gave crystals approaching to a platy habit, notably solochrome-yellow YS (C.I. 197) and alizarin-brown (C.I. 167). In some cases where the dye was insufficiently soluble in the cold to give habit modifications positive effects could be observed on crystallising hot solutions saturated with the dye.

Dye Adsorption, and the Structure of Sodium Nitrate Crystals.—Examination of a model of the structure of sodium nitrate, built according to the *X*-ray crystal structure deduced by Wyckoff [3] and revised by Tahvonen,[4] shows that the planes most steeply inclined to the usually modified face {0001} are $\{10\bar{1}0\}$ and $\{11\bar{2}0\}$ and $\{10\bar{1}1\}$, $\{10\bar{1}2\}$, and {1014} progressively less steeply inclined. Owing to the trigonal symmetry, detectable pleochroism cannot be expected in crystals modified by adsorption of dye on these forms, or on any other forms the planes of which are repeated threefold about the zone axis. In conformity with this, pleochroism in the {0001} sections of modified sodium nitrate crystals was never observed. There was therefore no possibility of directly deducing planes of dye adsorption as before.[5] It is, however, possible to account for dye adsorption by examining the degrees of coincidence between the polar groups of dye molecules and the ionic sites of the above crystal planes drawn to scale. It was concluded that of the above planes $\{10\bar{1}2\}$ and $\{11\bar{2}0\}$ are apparently most suitable for dye adsorption. As an example, Fig. 1 is a scale drawing of the $\{10\bar{1}2\}$ plane, with the dye molecule " EJ " (α-naphthylamine-5 : 7-di-sulphonate→β-naphthylamine-7-sulphonate→β-naphthol-3 : 6-disulphonate) superimposed. The coincidences between nitrate ion sites and sulphonate groups are remarkably good; this was noticed before the habit-modifying power of the dye was tested. The dye was found to be insoluble in cold saturated sodium nitrate solution, but dissolved in hot saturated solution and brought about the expected strong modification to {0001} plates on cooling the solution.

Two examples of crystal-habit modification of sodium nitrate with triphenylmethane dyes are of interest in view of the inferences as to the structures of the dyes concerned which may be made: (*a*) with ink-blue (*b*) with acid-green.

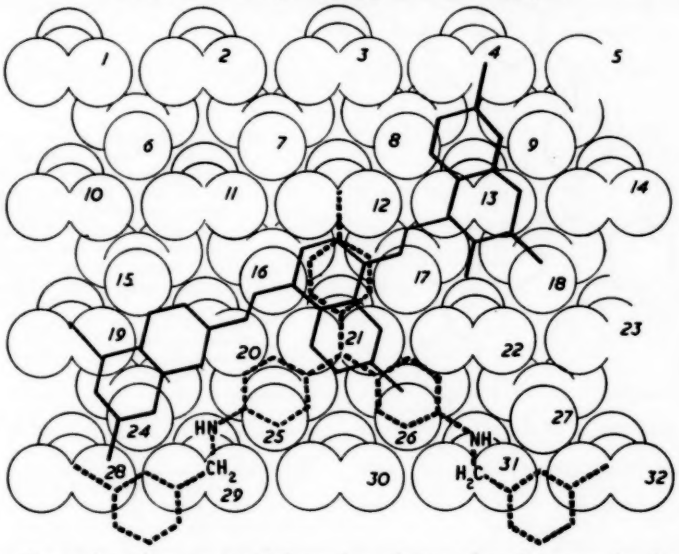
Modification of sodium nitrate with (a) *ink-blue* (C.I. 706). Samples of ink-blue AS manufactured by direct sulphonation of aniline-blue (triphenylated pararosaniline) were

[2] Buckley, *Z. Krist*, 1934, *A*, **88**, 381; *Mem. Proc. Manchester Lit. Phil. Soc.*, 1939, **83**, 31.
[3] Wyckoff, *Phys. Rev.*, 1920, **16**, 149.
[4] Tahvonen, *Ann. Acad. Sci. Fenn., Ser. A* 1, *Math. Phys.*, 1947, **42**, 244.

strongly soluble in saturated sodium nitrate solution and brought about crystallisation of the salt as aggregates of {0001} platy crystals. Samples prepared by Sandmeyer's process [6] were, however, almost completely insoluble in saturated sodium nitrate solution and did not affect the crystal habit. It was therefore suspected that the former sample had a higher degree of sulphonation than the latter, which was known to be trisulphonated.

Comparison of the dye structure with the ionic pattern of sodium nitrate {11$\bar{2}$0} showed clearly that, in addition to an exact fitting of the *para*-sulphonate groups of the *N*-phenyl

FIG. 1. *Dye EJ (solid outline) and acid-green GG (broken outline) on sodium nitrate* {10$\bar{1}$2}. *Nitrate ions lie in a plane steeply inclined to the paper.*



radicals on nitrate ion sites, *meta*-sulphonation of two phenyl groups in the rosaniline nucleus would exactly fit the nitrate ion pattern of the plane (Fig. 2). So would *ortho*-sulphonation of one of the *N*-phenyl groups. A pure sample of the Sandmeyer dye previously tested was further sulphonated for 1 hr. at 110° with 10% oleum, and a product apparently identical with ink-blue AS, in both its solubility and habit-modifying powers, was obtained. Analysis indicated about 5 sulphonate groups per molecule. It was evident that the dyes classified under C.I. No. 706 are likely to be of differing sulphonation, and consequently crystal-habit modifying activity, according to their method of preparation. Differences in degree of sulphonation are likely to be responsible in part at least for the large variations in activity of specimens of this dye from different sources observed by Buckley in his investigations with various salts.[7]

(b) *Acid-green M and GG extra* (C.I. Nos. 669 and 670). These two *N*-benzylated diaminotriphenylmethane derivatives were rather less active habit-modifiers than ink-blue, giving platy {0001} crystals on careful crystallisation from fairly concentrated dye solutions in saturated sodium nitrate solution (approx. 0·5% by wt. of dye).

The work of Fierz-David and others [8] has indicated that *meta*-sulphonation expresses correctly the sulphonation of the benzyl groups instead of the *para*-sulphonation shown in the Colour Index formulæ of these dyes. In conformity with this view, it was found

[5] Whetstone, *J.*, 1956, 4841; preceding paper.
[6] Geigy and Co., B.P. 12,720/1892.
[7] Buckley, *Proc. Manchester Lit. Phil. Soc.*, 1951, **92**, No. 6, 1.
[8] Fierz-David and Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publ. Inc. New York, 1949, p. 305.

impossible, by using *para*-sulphonated models, to obtain satisfactory agreements with {11$\bar{2}$0} or {10$\bar{1}$2}, but by using *meta*-sulphonated models the three sulphonate groups could easily be located accurately all at once on nitrate ions of the latter plane (Fig. 1).

Crystal-habit Modifications of Ammonium Sulphate.—With ammonium sulphate, as with potassium nitrate, differences in the appearances of {001} modified crystals according to the dye responsible would be expected if any tendency to pseudohexagonal twinning is

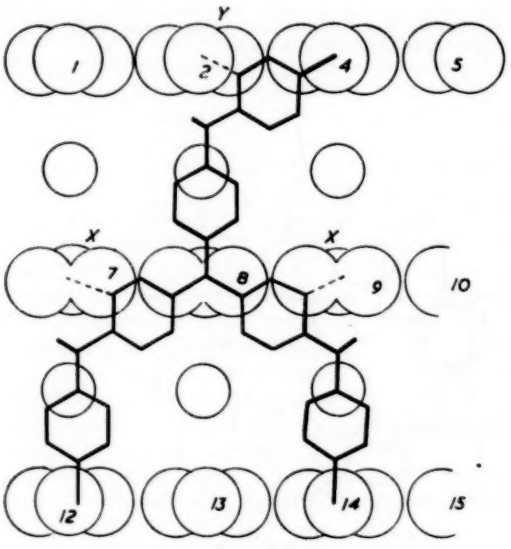


FIG. 2. *Ink-blue AS on sodium nitrate* {11$\bar{2}$0}. *Single circles are sodium ions. Nitrate ions are in a plane perpendicular to the paper and are represented edgeways, the oxygen atoms being shown. The broken lines at XX indicate* ortho-*sulphonation of the rosaniline nucleus. The broken line at Y indicates* ortho-*sulphonation of one N-phenyl group.*

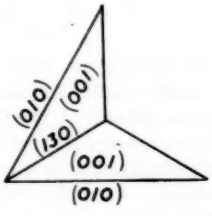


FIG. 3. *Derivation of " arrowhead " twins with tartrazine.*

present, but in fact no variation in the modified ammonium sulphate crystals comparable with those encountered with potassium nitrate was observed. No pleochroism should be obtainable from {001} modified ammonium sulphate crystals owing to their pseudohexagonal structure, even in the absence of twinning, if simultaneous dye adsorptions on sets of planes related by the pseudosymmetry have occurred.

Examination of ammonium sulphate crystals grown in the presence of some dyes showed that habit modifications could readily be obtained to give {010} platy rectangular crystals, or rectangular tablets. Other dyes gave very thin flexible hair-like needles, which apparently represent the ultimate habit-modification with very strong modifiers. These highly modified crystals are probably produced by the superimposition of the {001} effect on the {010} modification—it is not certain whether they are flattened on {001} or {010} since they were too thin for optical examination and too fragile to withstand manipulation. Crystallisation with low concentrations of these dyes invariably yielded {010} plates, but the {001} modification must have contributed considerably to the formation of the thin needles.

The pseudohexagonal symmetry of ammonium sulphate only once became evident in the formation of " arrowhead twins " from a saturated solution containing tartrazine on very long standing in a closed container; presumably the fine fibrous {001} modified crystals first deposited were unstable with respect to larger crystals, and dissolution of the former was followed by the very slow growth of the arrowhead twins. The plane of twinning was {130}, and the crystals were flattened on {001} (see Fig. 3).

It is noteworthy that azo-dyes containing a β-naphthol- or β-naphthylamine-3 : 6-disulphonate component usually appear to be especially effective as habit-modifiers for ammonium sulphate and give the {001} type of modification; quite a long list of these dyes can be compiled (see Table). It is thus probable that the inter-sulphonate distance in this

Some crystal-habit modifications of ammonium sulphate with dyes.

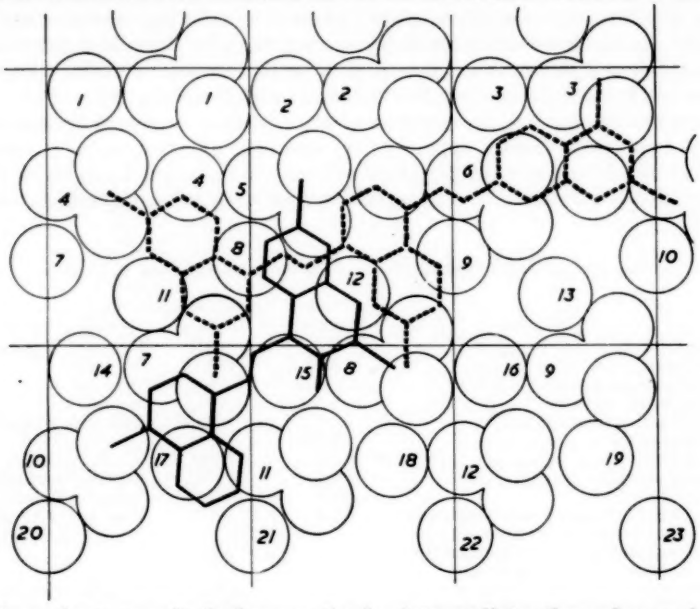
No.	Dye	Solubility *	Habit modification	Description of crystals
C.I. 184	Amaranth	Sol.	{001}	Fine, flat, soft needles
,, 188	Chromotrope 2B	Sol.	{001}	,, ,,
,, 197	Solochrome-yellow YS	Sol.	{001}	,, ,,
,, 315	Naphthol-black B	V.S.S.	{001}	Needles
,, 320	Biebrich Patent-black BO	Sol.	{001}	Fine, flat, soft needles
,, 438	Trypan-red	S.Sol.	{001}	,, ,,
,, 640	Tartrazine	Sol.	{001}	,, ,,
,, 692	Acid-magenta	Sol.	{010}	Rectangular plates
,, 706	Ink-blue AS	S.S.	{010}	Rectangular tablets, plates
BB	α-Naphthylamine-2-sulphonate→β-naphthol-3 : 6-disulphonate	S.S.	{001}	Fine, flat, soft needles
BA	α-Naphthylamine-4-sulphonate→β-naphthol-3 : 6-disulphonate	Sol.	{001}	,, ,,
BIF	α-Naphthylamine-3 : 6-disulphonate→β-naphthol-3 : 6-disulphonate	S.S.	{001}	Acicular, flattish
DIF	α-Naphthylamine-3 : 6-disulphonate→β-naphthol-4-sulphonate	Sol.	{001}	Fine, flat, soft needles
AIF	α-Naphthylamine-3 : 6-disulphonate→β-naphthol-6-sulphonate	S.S.	{001}	Acicular, flattened
GA	α-Naphthylamine-4-sulphonate→β-naphthylamine-3 : 6-disulphonate	Sol.	{001}	Fine, flat, soft needles
GB	α-Naphthylamine-3 : 6-disulphonate→β-naphthylamine-3 : 6-disulphonate	S.S.	{001}	Fine, soft needles
GC	Sulphanilic acid→β-naphthylamine-3 : 6-disulphonate	Sol.	{001}	Fine, flat, soft needles
HC	α-Naphthylamine-3 : 6-disulphonate→α-naphthol-4-sulphonate	S.S.	{001}	Fine needles
HD	Sulphanilic acid→H-acid	Sol.	{001}	Fine, flat, soft needles
HE	α-Naphthylamine-4-sulphonate→H-acid	Sol.	{001}	,, ,,
EJ	β-Naphthylamine-5 : 7-disulphonate α-naphthylamine-7-sulphonate→β-naphthol-3 : 6-disulphonate	Sol.	{001}	,, ,,
E2E	α-Naphthylamine-3 : 6 : 8-trisulphonate →α-naphthylamine-7-sulphonate→β-naphthol-3 : 6-disulphonate	Sol.	{001}	,, ,,
E2C	α-Naphthylamine-3 : 6 : 8-trisulphonate →α-naphthylamine→β-naphthol-3 : 6-disulphonate	Sol.	{001}	,, ,,

* S = soluble; S. sol. = slightly soluble; V.S.S. = very slightly soluble.

type of dye intermediate is reproduced accurately in some of the inter-sulphate ion distances in the ammonium sulphate structure. Fig. 4 illustrates the fitting of models of amaranth and the bisazo-dye " EJ " on to {100}. The structural determination of ammonium sulphate used was due to Ogg.[9] More than this simple correspondence of the 3 : 6-sulphonate groups of naphthalene with ionic sites is necessary, however, to give habit

[9] Ogg, *Phil. Mag.*, 1928, **5**, 354.

FIG. 4. *The bisazo-dye EJ (broken outline) and amaranth (solid outline) on ammonium sulphate {100}. Single circles are ammonium ions. Sulphate ions are shown in projection perpendicular to the paper.*



modifications of any magnitude, because the dye intermediates themselves such as R-salt have but a negligible effect on the crystal habit of ammonium sulphate.

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863. *Infrared Spectra and Polar Effects. Part VII.* Dipolar Effects in α-Halogenated Carbonyl Compounds.*

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The carbonyl frequencies of α-halogenated ketones, esters, and amides are discussed in relation to their steric arrangements and it is shown that a number of otherwise anomalous frequencies can be explained on the basis of intramolecular dipolar effects.

IN a previous communication [1] it was shown that the carbonyl frequencies of certain ω-chloroacetophenones vary systematically with the steric arrangements of the oxygen and chlorine atoms. The carbonyl frequency is raised about 20 cm.$^{-1}$ above that of acetophenone when these atoms are in a *cis*-configuration and near to each other, but it is essentially unaltered when they are in a *gauche* configuration and well separated. This is of course very similar to the well-known cases of α-bromo-keto-steroids [2] and α-chloro-*cyclo*hexanones [3] in which equatorial substitution of the halogen atom raises the carbonyl

* Part VI, *J.*, 1957, 863.

[1] Bellamy, Thomas, and Williams, *J.*, 1956, 3704.

[2] Jones, Ramsey, Herling, and Dobriner, *J. Amer. Chem. Soc.*, 1952, **74**, 2828; Jones, *ibid.*, 1953, **75**, 4839; Dickson and Page, *J.*, 1955, 447.

[3] Inayama, *Pharm. Bull. (Japan)*, 1956, **4**, 198; Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2301; Corey, Topie, and Wozniak, *ibid.*, 1955, **77**, 5415; Corey and Burke, *ibid.*, p. 5418.

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frequency whereas axial substitution does not. It has been tentatively suggested that this behaviour is due to dipolar or field effects [4,5] and this possibility has now been further studied.

Intermolecular field effects are well known and probably constitute one of the main causes of the frequency shifts which accompany changes of state. In acetone, for example, the fall in the carbonyl frequency from 1738 in the vapour to 1715 cm.$^{-1}$ in the liquid can be attributed to a partial orientation of the $\overset{+}{\text{C}}=\overset{-}{\text{O}}$ dipoles so that the positively charged carbon of one molecule is near to the negatively charged oxygen of another.[6] This leads to an increased bond polarity from induced charges, and the frequency falls. This is supported by the higher boiling point of acetone than of related hydrocarbons. However, little consideration appears to have been given to the possibility of intramolecular effects of the same type. In any molecular structure in which a charged atom is brought near in space to a readily polarisable carbonyl-oxygen atom a mutual induction of charges is likely to occur, which will alter the bond polarities and frequencies. In α-halogenated ketones in which a negatively charged halogen approaches near to the carbonyl-oxygen atom the induced charges would diminish the carbonyl bond polarity so that the frequency would rise in the way observed. Also, the size of the resulting shift would be an inverse function of the distance apart of the interacting atoms and so would depend directly on the steric arrangement of the molecule. This is an important distinction from purely inductive effects which may also be present, as these operate along the bonds and are independent of the molecular geometry. It has already been suggested [5,7] that the abnormal carbonyl frequencies of 21-acetoxy-20-keto-steroids may arise in this way, and we have now studied the behaviour of a further range of α-halogenated carbonyl compounds, differing in their degree of halogenation and in the steric resistance they offer to rotational isomerism, to see how far the results are consistent with a similar interpretation.

Experimental and Results

Samples were examined in either a Grubb-Parsons S.3A double-beam spectrometer with a sodium chloride prism, or a Grubb-Parsons G.S.2 single-beam instrument with a 2400 lines/inch N.P.L. replica grating. The carbonyl frequencies of all the compounds listed were checked by runs against a standard carried out at the same time. For frequencies between 1770 and 1690 cm.$^{-1}$ acetone in carbon tetrachloride (1719 cm.$^{-1}$) was used as standard, and for higher frequencies acetyl chloride vapour (1821 cm.$^{-1}$). The precision of measurement is therefore rather better than ± 2 cm.$^{-1}$. This has resulted in some minor discrepancies between the values now reported for ω-chloroacetophenones in the condensed phase and those given earlier.[1] However, this is due to a small constant calibration error in the earlier work which in no way affects the conclusions.

Conventional hot and cold cells were used as necessary for the examination of vapours, molten films, or crystalline forms. Liquids were studied at a stepwise series of temperatures, and changes in the carbonyl intensities recorded. Measurements on the relative intensities of individual bands were also made on solutions of similar concentration in solvents of different polarity. The results are summarised in Tables 1 and 3.

The trifluoroacetyl halides were fractionated until no further changes could be detected in their vapour spectra. All the ketones studied of sufficient volatility were checked for purity by vapour-phase chromatography. In a few instances it proved virtually impossible to obtain an absolute purification of the main component, but the impurities were in each case reduced to a level at which they would not influence the observed carbonyl frequencies. These cases were chloroacetone (less than 1% of dichloroacetone), 1 : 1-dichloroacetone (0·5% of chloroacetone; 2% of trichloroacetone), and *tert.*-butyl chloromethyl ketone (4% of *tert.*-butyl dichloromethyl ketone).

[4] Bellamy and Williams, *J.*, 1957, 861.
[5] Jones and Sandorfy, "Chemical Applications of Spectroscopy," Interscience, New York, 1956, p. 479.
[6] Wheland, "Resonance in Organic Chemistry," Wiley, New York, 1955, p. 52.
[7] Bellamy and Williams, *J.*, 1957, 863.

Halogenated ketones prepared in this laboratory were made as follows: Chloroacetone was prepared by the action of sulphuryl chloride on acetone, and *tert.*-butyl chloromethyl ketone by that of chlorine on *tert.*-butyl methyl ketone. The 1 : 1-dichloro-derivatives of these were made by the action of chlorine on the monochloro-derivatives. Trifluoroacetyl chloride and bromide were obtained by reaction of the acid with benzoyl chloride and with phosphorus pentabromide respectively. Trifluoroacetyl fluoride was produced by reaction of the acid with KHF_2 and benzoyl chloride, and the iodide by treatment of the chloride with hydriodic acid. Carbonyl bromide was obtained directly by interaction of carbon monoxide and bromine in sunlight.

Discussion

(I) *α-Halogenated Ketones.*—The ω-chloroacetophenones have been shown to exhibit rotational isomerism which gives rise to two carbonyl frequencies, and the higher of these has been assigned [1] to the form in which the chlorine atom is *cis* with respect to the carbonyl oxygen and therefore near to it in space. This assignment rests in part on the analogy with the α-halogeno-keto-steroids and also on the fact that the higher frequency is associated in all cases with the form which is more stable in the liquid and the solid state. Dipole-moment studies have established that the more polar *cis*-configuration is the stable form under these conditions in chloroacetone.[8,9] However, as some discrepancies appeared to arise with the assignments for chloroacetone itself (see below), we have sought further confirmation of the configurations of the ω-chloroacetophenone isomers by studying the changes which occur in the relative intensities of the individual carbonyl bands in solvents of different polarity. It is well known that solvents of high dielectric constant favour the more polar forms of rotational isomers so that the carbonyl absorption which corresponds to this form should increase sharply at the expense of the other on changing from a non-polar to a polar solvent. Table 1 shows that marked changes of this type do occur and that the higher-frequency carbonyl absorption is intensified in acetonitrile as compared with carbon tetrachloride in all cases. This again associates the higher of these two frequencies with the more polar *cis*-form in which the oxygen and halogen atoms are close together. We have also extended our study of this series to include the spectra of the vapours. In general, simple α-halogenated ketones exist only in the *gauche* configuration in the vapour state [8,9] (see below), and this has been ascribed to the predominance of the electrostatic repulsion between the oxygen and chlorine atoms over the steric repulsion exerted by the alkyl group.[8]

This appears to be true of ω-chloroacetophenone itself which shows only a single carbonyl absorption at 1709 $cm.^{-1}$, at the same point as acetophenone itself. However, in ωω-dichloroacetophenone two bands are shown at 1729 and 1707 $cm.^{-1}$. The introduction of the second chlorine atom has therefore increased the proportion of the more polar form. Doubling of the carbonyl absorption is also found in the vapour spectra of many substituted ω-chloroacetophenones. This is particularly marked in the *ortho*-substituted compounds in which the influence of steric repulsions would be at a maximum.

We have also studied a series of acetone derivatives with various degrees of chlorination. Of these, perhaps the most important is chloroacetone itself, which has been previously studied by Mizushima *et al.*[8] The values for the carbonyl frequencies of this compound in various states are listed in Table 1, and, with the exception of the solid state these agree very well with the previous results. Dipole-moment and spectroscopic studies have shown that the more polar *cis*-form (I) is the more stable in the liquid and solid states whereas form (II) (*gauche*) appears to be favoured in the vapour. However, Mizushima *et al.*[8] have assigned the 1745 and 1725 $cm.^{-1}$ absorptions of the liquid to forms (II) and (I), respectively. This is the inverse of what would be expected from the dipolar considerations above, but is in accord with the 1718 $cm.^{-1}$ frequency which they report for the solid state.

[8] Nakagawa, Ichishima, Kurakani, Miyazawa, Shimanouchi, and Mizushima, *J. Chem. Phys.*, 1952, **20**, 170.

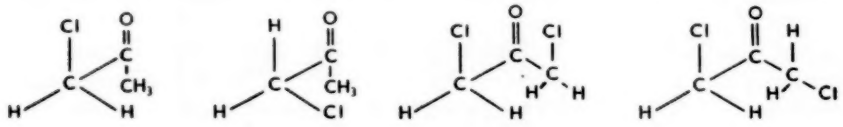
[9] Mizushima, Shimanouchi, Miyazawa, Ichishima, Kuratani, Nakagawa, and Shida, *ibid.*, 1953, **21**, 815.

TABLE 1. *Frequencies in the carbonyl region (cm.$^{-1}$).*

Substance	Vapour	Liquid	Solid	Solution in CCl_4	Solution in $CH_3{\cdot}CN$
$COMe_2$	1738	1715	—	1719	1715
COMeEt	1739	1719	—	1723	1715
$COMePr^i$	1734	1715	—	1719	1711
$COMeBu^t$	1726	1711	1705	1711	1704
$COMeBu^i$	1736	1717	—	1721	1712
$CMe_2{\cdot}CO{\cdot}CHMe_2$	1722	1708	—	1709	1702
$CH_3{\cdot}COPh$	1709	1687	1682	1692	1688
$Ph{\cdot}CO{\cdot}CH_2Cl$	1709	1709, 1693 0·75	1703	1715, 1696 ·1·58	1710, 1694 0·52
$Ph{\cdot}CO{\cdot}CHCl_2$	1729, 1707 1·35	1707, 1690 0·66	1709	1716, 1692 1·29	1713, 1695 0·19
p-$Cl{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$	1709	1707, 1695 1·00	1696	1715, 1696 2·22	1711, 1695 0·54
3 : 4-$Cl_2C_6H_3{\cdot}CO{\cdot}CH_2Cl$	1709	1710, 1694 0·73	1708	1718, 1698 2·25	1714, 1698 0·59
2 : 4- ,,	1720	1723, 1707 >1·31	1713	1733, 1710 $\geqslant$3·28	1727, 1711 $\leqslant$0·82
2 : 5- ,,	1721	1728, 1710 >1·35	1716	1736, 1713 $\geqslant$2·42	1731, 1714 $\leqslant$0·77
2 : 4 : 6-$Cl_3C_6H_2{\cdot}CO{\cdot}CH_2Cl$	1731	1741, 1721 0·80	1735	1747, 1722 1·23	1739, 1721 0·45
$CH_3{\cdot}CO{\cdot}CH_2Cl$	1743	1743, 1725 0·98	1742, 1728	1752, 1726 2·75	1744, 1726 0·81
$CH_3{\cdot}CO{\cdot}CHCl_2$	1756, 1722 0·10	1740	1732 cryst. 1742 glassy	1743, 1724 <0·15	1745, 1716 <0·15
$CH_2Cl{\cdot}CO{\cdot}CH_2Cl$	1746	1755, 1742,1728	1745	1746, 1730 0·80	1752, 1744 $\geqslant$1·39
$CHCl_2{\cdot}CO{\cdot}CHCl_2$	1770	1773, 1762 1·21	1770, 1739 cryst. 1768, 1733 glassy	1774, 1764 2·00	1772, 1758 1·07
$CCl_3{\cdot}CO{\cdot}CCl_3$	1784	1778, 1750 0·37	1779, 1757, 1745	1780, 1751 0·35	1780, 1751 $\leqslant$0·49
$CH_2Cl{\cdot}COPr^i$	1732	1732, 1720 <0·66	1722	1740, 1720 1·90	1734, 1719 $\leqslant$0·48
$CH_2Cl{\cdot}COBu^t$	1733	1726, 1712 <0·10	1717	1732, 1713 $\leqslant$0·30	1725, 1709 $\leqslant$0·08
$CHCl_2{\cdot}COBu^t$	1750	1743, 1731 >1·59	1730	1745, 1734 1·13	1742, 1729 $\geqslant$3·03

Notes. (1) Only major peaks are recorded. Inflexions and minor bands are often observed especially in the aliphatic compounds in the solid state.
(2) The figure after the frequency, when quoted, refers to ε (lower frequency)/ε (higher frequency), where ε is the apparent max. extinction coefficient.

In view of this discrepancy we have studied this compound in some detail. As indicated earlier, we have been unable to reproduce their findings for the solid state, but find instead a main peak at 1728 cm.$^{-1}$ with a shoulder at 1742 cm.$^{-1}$. This observation has been checked a number of times both at −80° and at liquid-nitrogen temperatures, and care has been taken to ensure that the sample was truly crystalline and not a glass, by examination through polarisers. Under these conditions only one rotational isomer can be



(I) (II) (III) (IV)

present and the splitting must arise either from crystal splitting effects or from the presence of a unit cell of two or more molecules in which the carbonyl groups are in different environments. As both frequencies are higher than the 1725 cm.$^{-1}$ liquid-state frequency they are almost certainly derived from the form absorbing at 1745 cm.$^{-1}$, so it appears reasonable to reverse the original assignments and identify the 1745 cm.$^{-1}$ absorption of the liquid with the *cis*-form (I). This is fully supported by the results of temperature-dependence studies. As the temperature of the liquid is raised, the intensity of the 1725 cm.$^{-1}$ band increases at the expense of the 1745 cm.$^{-1}$ band, indicating that the latter is to be associated with the more stable form in this state (*i.e.*, *cis* as in I). Finally, a very marked change in the relative intensities of these bands occurs on passing from solutions in carbon tetrachloride to those in acetonitrile. The intensification of the 1745 cm.$^{-1}$ band in the latter, more polar, solvent again identifies this band with the more polar form (Table 1). Whatever the origins of the splitting of the carbonyl absorption in the crystal, these findings are clear evidence for the presence of genuine rotational isomers, and the revised assignments are fully consistent with the concept of dipolar interaction outlined above.

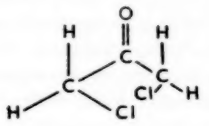
The behaviour of 1 : 1-dichloroacetone is in many ways very similar. The more polar form could exist either with one chlorine atom eclipsed by the oxygen or in a staggered arrangement similar to (X*a*). From the electrostatic point of view these alternatives are approximately equivalent, so that it is to be expected that the observed frequencies will be closely parallel to those of chloroacetone itself. It will be seen that this is generally so, although there is a marked intensification of the higher-frequency absorption in the liquid. In the vapour phase the main carbonyl absorption at 1756 cm.$^{-1}$ corresponds to a more polar configuration. This band is accompanied by a weak shoulder at 1722 cm.$^{-1}$. This is at a lower frequency than would be expected from a configuration in which both chlorine atoms were *gauche* with respect to the carbonyl oxygen atom which should be similar to that of methyl *iso*propyl ketone in the vapour state (1734 cm.$^{-1}$). There is little or no change in the relative intensities of these bands with temperature, so it is likely that the weak 1722 cm.$^{-1}$ absorption represents a combination band from lower-frequency fundamentals. In the crystalline state the main carbonyl absorption is at 1732 cm.$^{-1}$, and this is clearly the more polar form and corresponds to the liquid frequency of 1740 cm.$^{-1}$. Although the band is not doubled it is accompanied by a series of minor weak absorptions on both sides which probably also arise from overtone or combination bands.

It is interesting to compare these findings with those for 1 : 3-dichloroacetone. This compound has been previously studied by Daasch and Kagarise,[10] who demonstrated the existence of rotational isomers but did not attempt to associate any particular bands with individual isomers. Our own findings are listed in Table 1 and show only minor differences

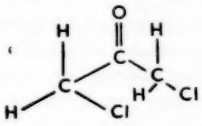
[10] Daasch and Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 6156.

from theirs. Unfortunately, the spectra in the carbonyl region of the liquid and solid forms are very complex and show a number of weak bands in addition to the main absorptions. This renders interpretation difficult, but the results would nevertheless appear to be reasonably consistent with the theory of dipolar interactions outlined earlier. On this basis 1 : 3-dichloroacetone would be expected to show three main peaks corresponding to forms (III), (IV), and (V), as form (VI) is almost certainly excluded on steric grounds.

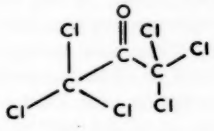
In the liquid state the main carbonyl absorptions occur at 1755, 1742, and 1728 cm.$^{-1}$ with weak bands at 1785 and 1722 cm.$^{-1}$. Both the 1755 and the 1785 cm.$^{-1}$ band diminish in intensity with increase in temperature so that either could be associated with form (III). However, the size of the frequency shifts of the 1755 cm.$^{-1}$ band as compared with that of



(V)



(VI)



(VII)

liquid acetone is of the order to be expected from two *cis*-chlorine atoms, and this appears the most likely choice. This is supported by the fact that the most intense absorption in the crystal, which is likely to be form (III), is at 1745 cm.$^{-1}$, which would correspond to a similar fall of the 1755 cm.$^{-1}$ band with change of state to that which occurs in the chloroacetophenones. The 1785 cm.$^{-1}$ band could well arise as a combination of the strong absorptions [15] at 1051 and 732 cm.$^{-1}$. The persistence of the 1755 cm.$^{-1}$ band in acetonitrile and its disappearance in the less polar carbon tetrachloride also support the assignment to the most polar configuration. The 1742 cm.$^{-1}$ band would then arise from form (IV), and it represents the most intense absorption in the liquid and solution states. As the temperature rises the intensity of this band increases with respect to the 1755 cm.$^{-1}$ and falls with respect to the 1728 cm.$^{-1}$ absorption which indicates a form of intermediate stability between (III) and (V). The 1728 cm.$^{-1}$ band as indicated above is the least stable form in the liquid and is therefore probably associated with form (V), and the absence of any notable frequency shift over that of acetone is in line with this assignment. It is possible that the 1722 cm.$^{-1}$ band which shows similar temperature dependence could be due to this form, but this band is much weaker and is more likely to be a combination band of the absorptions at 951 and 765 cm.$^{-1}$. These assignments are supported by the intensity changes which occur on passing from acetonitrile to carbon tetrachloride. The 1730 cm.$^{-1}$ band, for example, is very weak in acetonitrile and strong in carbon tetrachloride, as would be expected from the least polar configuration. In the solid a multiplicity of peaks again occurs many of which must be combination bands as only one configuration is possible. However, the main peak in both the cubic and the needle crystalline modification is at 1745 cm.$^{-1}$ which, allowing for the frequency fall accompanying a change of state, is consistent with its assignment to the expected *cis*/*cis*-form (III). In the vapour phase the stability relations of compounds of this type appear to be the reverse of those for the liquid state and, as with chloroacetone and ω-chloroacetophenone, the main frequency of 1 : 3-dichloroacetone (1743 cm.$^{-1}$) is very close to that of acetone itself and is clearly due to the least polar form (V). However, it is accompanied in this case by a weak shoulder at 1767 cm.$^{-1}$. After allowance for the rise of 23 cm.$^{-1}$ which follows a change of state in acetone from liquid to vapour, this probably corresponds to the liquid frequency of 1742 cm.$^{-1}$ and indicates the presence of a small proportion of form (IV).

s-Tetrachloroacetone has also been studied. Steric effects are likely to be considerable in this molecule and one must also expect an intensification of any combination bands associated with the C–Cl stretching modes at lower frequencies. It is, however, unlikely on steric grounds that any modification can exist in which all the halogen atoms are *gauche*

with respect to the carbonyl oxygen, and in accordance with this idea no carbonyl frequency is found which corresponds to that of acetone. Two bands are observed in the liquid at 1773 and 1762 cm.$^{-1}$. These are markedly temperature-dependent, indicating rotational isomerism, and solvent studies identify the higher frequency with a more polar form. It is possible, therefore, that the first is derived from a form analogous to (III) in which two halogen atoms are *cis* to the carbonyl oxygen atom, and the second from a form similar to (IV). However, it is also possible in view of the considerable steric hindrances that skewed configurations may be involved. However, the observation that in the solid and in the vapour form the carbonyl frequencies remain high is consistent with the view that a form in which both hydrogen atoms are *cis* with respect to the carbonyl oxygen atom does not exist.

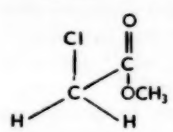
Hexachloroacetone has also been examined. As a symmetrical molecule this can exist in only one form, and an elevated carbonyl frequency is to be expected. The main carbonyl band in all states occurs in the range 1778—1784 cm.$^{-1}$ but is accompanied by a weaker absorption near 1750 cm.$^{-1}$. The behaviour of the latter band with changes of temperature or of solvent is in marked contrast to that shown by genuine carbonyl absorptions arising from rotational isomerism. Practically no change of the relative intensities of the two bands is shown under these conditions, and the 1750 cm.$^{-1}$ absorption is therefore almost certainly a combination band. Strong bands are found at 1095 and 656 cm.$^{-1}$ which would account for this absorption. As *s*-tetrachloroacetone is apparently precluded from existing in a form in which all the chlorine atoms are *gauche* to the carbonyl oxygen, it is likely that hexachloroacetone will assume some type of configuration such as in (VII) in which one halogen atom is *cis* to the carbonyl whilst the other CCl_3 group takes up a skew arrangement with two halogen atoms each at 60° to the C=O axis.

From the point of view of simple electrostatic interactions this latter pair would behave in the same way as one chlorine in the *cis*-position. The observed carbonyl frequencies should therefore correspond to compounds with two *cis*-chlorine atoms. In the vapour phase the 1784 cm.$^{-1}$ band is 29 cm.$^{-1}$ higher than the 1755 cm.$^{-1}$ liquid frequency of 1 : 3-dichloroacetone which has been assigned to a *cis*/*cis*-form. Allowance being made for the usual shifts which accompany change of state, this agreement is reasonable. However, the liquid (1778 cm.$^{-1}$) and solid (1779 cm.$^{-1}$) frequencies are both appreciably higher than would be expected on this basis. This may be due to residual inductive effects of the CCl_3 groups but could also arise from an intermolecular dipolar interaction between the carbonyl oxygen and the halogen atoms of other molecules in the condensed phases.

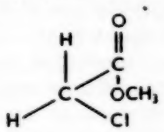
The factors which determine the relative stabilities of rotational isomers of α-halogenated ketones must be the electrostatic repulsion between the chlorine and oxygen atoms on the one hand and the steric repulsion between the chlorine atom and the other carbonyl substituent on the other.[8] In general, the former effect predominates in the vapour phase but the effect of dielectric constant makes the latter more important in the liquids and solids. It therefore seemed of interest to examine the rotational isomerism of ketones containing bulkier substituents to see how far this influenced the relative stabilities of the different isomers. We have accordingly studied chloromethyl *iso*propyl ketone and *tert.*-butyl chloromethyl ketone. It will be seen from Table 1 that in both cases the electrostatic repulsion effect predominates as before in the vapour phase and that, as with ω-chloroacetophenone, the carbonyl frequencies found in this state are the same as those of the parent ketones. In the liquid and solution two forms occur and the higher carbonyl frequency in each case is readily identified with the more polar *cis*-chlorine–oxygen configuration by the temperature-dependence behaviour, by the changes with solvents of different polarity, and by the solid-state frequencies. The latter again show the anomalous doubling observed in other cases, but the main absorption in each case can be identified with the higher liquid frequency. It would seem therefore that in monochlorinated compounds the steric repulsions of the *iso*propyl, *tert.*-butyl, and phenyl groups are insufficient to overcome the electrostatic repulsions and stabilise the *cis*-configurations in

the vapour phase. In *ortho*-substituted phenyl compounds, however, the situation is reversed and the more polar form predominates in the vapour. It is interesting to compare these findings with the results obtained in the *gem*-dichloromethyl compounds, in which the more polar isomer is the stable form in the vapour phase. It has been suggested above that in this series it is perhaps more probable that the polar forms will assume configurations analogous to (X*a*) rather than to (X) and from the point of view of electrostatic effects upon the carbonyl frequency the two forms are equivalent. The introduction of the second halogen atom has, however, increased the steric resistances to internal rotation, whilst the electrostatic repulsion forces remain approximately the same, so that the proportion of the more stable form is increased. Nevertheless, it remains difficult to understand why the more polar form of 1 : 1-dichloroacetone should appear exclusively in the vapour whereas in ωω-dichloroacetophenone in the same state both forms are found.

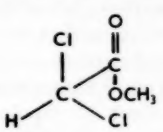
(2) *α-Halogenated Esters.*—The available data on α-halogenated esters indicate that they behave in a very similar way to the ketones. Studies on pure liquids [11] or in highly polar solvents [12] have given rather conflicting results as some mono- or di-halogenated esters show only one carbonyl absorption whilst others show two. This is probably due to the fact that the liquids themselves are highly polar, so that the concentrations of the less polar isomers would be much reduced. Josien and Callas,[13] using a high-dispersion instrument, have demonstrated the existence of rotational isomers in carbon tetrachloride solutions, and the observed frequencies are readily understandable on the basis of dipolar interaction. For example, methyl acetate absorbs at 1750 cm.$^{-1}$ and both methyl chloroacetate and methyl dichloroacetate show two bands at 1775 and 1750 cm.$^{-1}$. The higher frequency can be assigned to forms (VIII) and (X) (or X*a*) respectively whilst the lower corresponds to forms (IX) and (XI) and is the same as for methyl acetate. The trichloro-



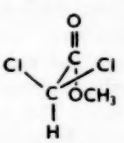
(VIII)



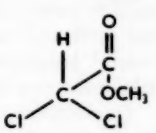
(IX)



(X)



(X *a*)



(XI)

derivative, in which either one halogen is *cis* to the carbonyl oxygen or two are in an electrostatically equivalent arrangement similar to (X*a*), confirms this, as it shows a single absorption at 1770 cm.$^{-1}$.

(3) *α-Halogenated Amides.*—The influence of α-halogen substitution on amide-carbonyl frequencies is difficult to study owing to limited solubilities and to hydrogen-bonding effects in the solids. Nevertheless it is clear that such effects follow a different pattern from those of the corresponding ketones or esters. In *N-n*-butylchloroacetamide, for example, the carbonyl frequency in carbon tetrachloride is the same as in the original amide and it is not until a second halogen atom is introduced that any frequency shift occurs.[14] Similarly, the di-*n*-butylamide absorbs only 9 cm.$^{-1}$ higher than the unchlorinated compound. This can be explained on the basis of dipolar interactions, as mesomerism leaves the nitrogen atom with an effective positive charge. The electrostatic repulsion between the chlorine and oxygen atoms is reinforced by the electrostatic attraction between the chlorine and nitrogen atoms; and the isomer in which the chlorine is *gauche* with respect to the carbonyl-oxygen atom is stabilised. This probability has been independently confirmed in the case of methyl chloroacetamide in which dipole-moment studies have shown that, in contrast to chloroacetone, the *gauche* configuration is the more stable in the liquid and the solid state and that the more polar isomer is almost non-existent in non-polar

[11] McBee and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 755.
[12] Bender, *ibid.*, 1953, **75**, 5986.
[13] Josien and Callas, *Compt. rend.*, 1955, **240**, 1641.
[14] Letaw and Groop, *J. Chem. Phys.*, 1953, **21**, 1621.

XUM

solvents.[15] Data on dihalogenated amides are limited, but the *NN*-di-*n*-butyl derivatives of dichloro-, difluoro-, and chlorofluoro-acetamide show the expected two carbonyl frequencies [14] which would arise from rotational isomerism. On the other hand, the corresponding secondary amides show only a single absorption throughout. This may be due to differences in steric effects in the two series but more work is required before any final conclusions are possible.

General.—The demonstration that in all the cases described above it is the more polar forms of α-halogenated ketones which show raised carbonyl frequencies is clear evidence for the existence of a stereospecific effect. This cannot be normal induction and is most easily explained as a simple electrostatic interaction across intramolecular space. This idea then allows a simple explanation of a number of otherwise anomalous carbonyl frequencies; *e.g.*, it explains the differences between the behaviour of α-monohalogenated ketones and amides, the presence of two carbonyl frequencies in partially chlorinated compounds and of only one in the fully chlorinated product, the absence of any further frequency rise when a second halogen atom is introduced at an α-position, and the occurrence of such a rise when it is introduced at the α'-position.

The data indicate clearly that the dipolar field effects are the major factors involved in frequency shifts in these cases. However, this does not imply that inductive effects are wholly absent. Some changes in the inductive effect must occur on passing through the series $CH_3 \longrightarrow CCl_3$ and the fact that mono-halogenated materials in the *gauche* configuration with respect to the chlorine and oxygen atoms show substantially the same frequencies as the unhalogenated compounds probably arises from the existence of weak field effects in this configuration also. These would be expected to be of opposite sign to those arising in *cis*-configuration so that they would roughly offset the increased inductive effect. The small frequency changes which sometimes follow the introduction of a third α-halogen atom may well arise in this way. Thus in methyl trichloroacetate the carbonyl frequency is 5 cm.$^{-1}$ lower than in the *cis*-disubstituted or monosubstituted materials [13] and ethyl trifluoroacetate absorbs at about 9 cm.$^{-1}$ higher than the difluoro-compound.[12]

Quantitative aspects. The concept of dipolar interactions appears to provide an adequate qualitative explanation for much of the above data, but it is desirable to show that interactions of this kind can lead to frequency shifts of approximately the same order of magnitude as those observed.

A very convenient means of estimating the magnitudes of inductive effects in molecules is provided by the theory of Smith, Ree, Magee, and Eyring.[16] In this method, a semi-classical approach is used to calculate the approximate net charges on the atoms in a molecule, it being assumed that the only electrical effects are inductive ones, operating along the bonds. To evaluate these charges, each atom in a particular bond is associated with two parameters, β and γ. The former can be calculated from the longitudinal bond polarisability, bond length, and Slater screening constant, and in, *e.g.*, a bond AB β_{AB} represents the inductive effect on the charge on atom A by the charge on atom B. The parameter γ_{AB}, which represents the charge on atom A before the effect of induction from B is considered, cannot easily be calculated from atomic and bond properties in a similar manner to β_{AB} but can instead be obtained from the observed moments of suitable molecules. These values can then be used for the calculation of charge distribution in other molecules containing the same links.

Smith *et al.* list values for β_{AB} for a number of bonds and also for γ_{AB} for the CF, CCl, CBr, and CI links. These values have been adopted for this work except that slight alterations have been made in the γ_{AB} figures because of the more accurate values for the dipole moments of the methyl halides now available.[17] Since the values of γ_{AB} depend on

[15] Mizushima, Shimanouchi, Ichishima, Miyazawa, Nakagawa, and Araki, *J. Amer. Chem. Soc.*, 1956, **78**, 2038.
[16] Smith, Ree, Magee, and Eyring, *ibid.*, 1951, **73**, 2263.
[17] "Dielectric Constants and Electric Dipole Moments of Substances in the Gaseous State," N.B.S. Circular No. 537, Nat. Bur. Stand., Washington, 1953.

the value of μ_{CH} in methane, the set corresponding to $\mu_{C^+H^-}$ 0·3 D have been chosen. γ_{OO} was calculated from the molecular dipoles of formaldehyde and carbonyl chloride, and the β parameter for the C–C bond was that suggested by Smith and Mortensen.[18]

TABLE 2.

Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)	Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)	Bond AB	β_{AB}	$\gamma_{AB} \times 10^{10}$ (e.s.u.)
H–C	0·13	−0·418	Cl–C	0·71	−2·40	I–C	1·29	−2·865
F–C	0·25	−1·91	Br–C	0·91	−2·55	O=C	0·45	−3·023

By using the constants in Table 2, the charge distributions for a number of RR'CO compounds were evaluated, and from these, the dipole moment of the C=O bond and, in some cases, the molecular dipole were deduced. The results are shown in Table 3 together with the observed molecular dipole, where available. It will be seen that this approach leads to resonable values for individual bond dipoles and that in the cases where the molecular dipole moment is known, the agreement between the observed and calculated values is good.

TABLE 3. (*All substances measured in the vapour phase.*)

Substance	μ_{CO} (D), calc.	$\mu_{molecular}$ (D): calc.	obs.	ν_{CO} (cm.$^{-1}$): obs.	mass-corr.	Substance	μ_{CO} (D), calc.	$\mu_{molecular}$ (D): calc.	obs.	ν_{CO} (cm.$^{-1}$): obs.
CH_2O ...	2·45	2·31	2·34	1744 [a]	1771	CF_3·COF ...	1·97	0·34	—	1901 [b]
COF_2	1·68	0·10	—	1928 [a]	1916	CF_3·COCl ...	2·16	1·07	—	1810 [b]
$COCl_2$ ...	2·09	1·18	1·19	1827 [a]	1822	CF_3·COBr ...	2·23	1·53	—	1838 [b]
$COBr_2$ ...	2·23	1·25	—	1826 [b]	1825	CF_3·COI	2·34	2·35	—	1812 [b]
COHF ...	2·01	1·77	—	1837 [f]	1850	CF_3·CHO ...	2·35	1·53	—	1788 [c]
COClF ...	1·93	1·23	—	1868 [a]	1860	CF_3·CO·CH_3	2·50	2·58	—	1780 [d]
CH_3·CHO	2·61	2·67	2·72	1752 [b]		CF_3·CO·CF_3	2·26	0·32	—	1825 [e]
$(CH_3)_2CO$	2·75	2·85	2·88	1740 [b]						

[a] Kagarise, *J. Amer. Chem. Soc.*, 1955, **77**, 1377. [b] This work. [c] Husted. [d] Whiffen. [e] R. N. Jones. [f] Wilkinson and Price, personal communications.

Frequencies of groups in the infrared region are usually sensitive to changes both in the electrical nature and in the mass of substituents. However, in the case of R'R'CO group Halford [19] has recently shown for all masses greater than about 12 when R is polyatomic, that the CO frequency is mass-insensitive and he has also supplied correction formulæ for when R is monatomic. Table 3 gives the observed carbonyl frequency and also the mass-corrected frequency when this is significantly different.

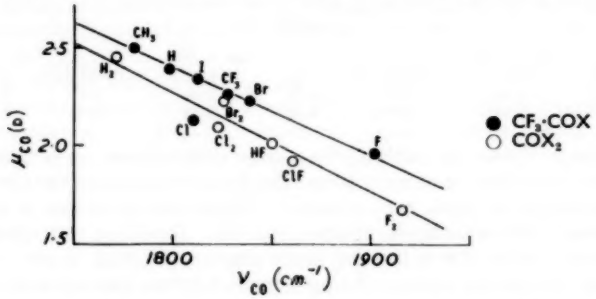
When the bond dipoles are plotted against the carbonyl frequencies, a simple relation is found (see Figure), as would be expected if the frequencies were directly related to the inductive effect of substituents on the carbonyl. The acetyl halide series has also been studied and gives a line parallel to that of the COX_2 line. However, the position of this line is sensitive to the choice of the sign of μ_{CH} in methane, lying below or above the COX_2 line for the two extremes of $\mu_{CH} \pm 0{\cdot}3$ D.

The CO bond dipoles of the trifluoroacetyl halide series in Table 3 have been calculated solely on the basis of induction through the bonds. It will be seen from the Figure that this line is diplaced from the basic carbonyl line by about 0·2 D, which we attribute to the intramolecular field effect from a fluorine atom in the *cis*-position to the carbonyl-oxygen atom.

It is possible to estimate the magnitude of the induced dipoles which would arise in this way. By taking the calculated CF and CO bond dipoles as 1·51 and 2·35 D, respectively, and the CF and CO longitudinal bond polarisabilities as $0{\cdot}96 \times 10^{-24}$ and $1{\cdot}99 \times 10^{-24}$ c.c. and assuming that point dipoles are located in the fluorine and oxygen atoms, it can be shown that μ_{CF} would be lowered by about 0·15 D and μ_{CO} by about

[18] Smith and Mortensen, *J. Amer. Chem. Soc.*, 1956, **78**, 3932.
[19] Halford, *J. Chem. Phys.*, 1956, **24**, 830.

0·19 D as a result of the dipolar interaction. The good agreement obtained is probably fortuitous, as the calculation is very much an approximation and takes no account of the likely influence of the other halogen atoms in *gauche* configurations. Nevertheless, it



indicates that a field effect of the type postulated would be likely to lead to frequency shifts of the general order of magnitude which is observed.

Thanks are offered to Drs. B. K. Howe and A. H. Ford-Moore for certain of the halogenated ketones. This work was carried out during the tenure by one of us (R. L. W.) of a Senior Research Fellowship of the Ministry of Supply.

E.R.D.E., Ministry of Supply, Waltham Abbey, Essex. [*Received, April 29th,* 1957.]

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864. *Researches on Monolayers. Part VI.* A Study of Reactions in Surface Films of Acetates and Ketones, and their Relation to Adsorption by Cellulose Acetate.*

By A. Cameron, C. H. Giles, and T. H. MacEwan.

Monolayers of cetyl acetate, cellulose triacetate, methyl stearyl ketone, and ethyl stearyl ketone have been spread on water and aqueous solutions of a variety of aliphatic and aromatic compounds; a mixed film of cellulose triacetate with a non-ionic "disperse" dye for cellulose acetate has also been examined. The molecular area and compressibility data show that in presence of water the ketone group has much weaker hydrogen-bonding power than the acetate group, and the films of the ketones are consequently expanded much less by all the solutes than the acetate films are. Highly ionised compounds, including sulphonated dyes, cause considerable expansion of the cellulose triacetate films, even though they have no affinity for the same material in bulk.

The results are used to interpret the mechanism of adsorption of solutes by cellulose acetates.

Previous papers in this series[1,2] have described various types of hydrogen-bonding reactions between monolayer molecules on water and solutes in the water beneath. The results in one case[2] were used to interpret the mechanism of adsorption of solutes by cellulose and cellulose acetate. The present investigation is an attempt to use reactions in monolayers in a more detailed manner to throw light on the mechanism of adsorption of solutes by cellulose acetates.

The substances spread as monolayers were cellulose triacetate, cetyl acetate, ethyl

* The Paper "Studies in monolayers. Part V" (*J.*, 1957, 3140) is regarded as Part V of this series.

[1] Giles and Neustädter, *J.*, 1952, 3806.

[2] Allingham, Giles, and Neustädter, *Discuss. Faraday Soc.*, 1954, **16**, 92.

stearyl ketone, methyl stearyl ketone, etc. The second and third have almost identical molecular area and compressibility as films (cf. Table 1), and their alkyl chains are nearly equal in length, but their polar groups differ in hydrogen-bonding properties. Thus they

TABLE 1. *Molecular areas, compressibilities, etc., of monolayers of acetates and ketones.*

Substrate (aq. soln.)	Films: Cetyl acetate				Films: Ethyl stearyl ketone			
	a *			*b* †	*a*			*b*
Water	24	40	21	0·4	25	29	24	0·5
Group I								
0·1M-Ethylene glycol	30	53	25	0·6	—	—	—	—
0·1M-Mesaconic acid	28	53	24	0·5	—	—	—	—
4·5M-Urea	45	75	35	1·4	29	—	25	0·67
0·1M-Ethyl methyl ketone	—	—	—	—	—	—	—	—
Group II								
0·1M-Benzenesulphonic acid	27	55	21	0·5	—	—	—	—
0·1M-Benzoquinone	27	55	21	0·5	—	—	—	—
0·1M-Phenol	60	90	47	3·0	—	—	—	—
0·1M-Pyridine	27	47	24	0·45	—	—	—	—
0·1M-Quinol	62	75	50	1·7	32	55	27	1·0
0·1M-Sucrose	25	—	18	0·5	—	—	—	—
Group III								
0·01M-Acid magenta	—	—	—	—	—	—	—	—
0·00025M-Pinacyanol	83	110	72	1·7	34	45	30	0·82
0·025M-2 : 2′-Dipyridyl	59	76	54	1·8	—	—	—	—
0·01M-Sulphato-ester dye	—	—	—	—	30	50	23	1·05
0·01M-Anthraquinone-2-sulphonic acid	—	—	—	—	—	—	—	—
Dispersol fast crimson B (mixed film)	—	—	—	—	—	—	—	—

Substrate (aq. soln.)	Films: Methyl stearyl ketone				Films: Cellulose triacetate			
	a			*b*	*a*			*b*
Water	21	26	20	0·2	37	60	34	0·4
Group I								
0·1M-Ethylene glycol	—	—	—	—	—	—	—	—
0·1M-Mesaconic acid	23	32	23	0·4	—	—	—	—
4·5M-Urea	—	—	—	—	70	87	63	1·15
0·1M-Ethyl methyl ketone	—	—	—	—	41	54	34	0·71
Group II								
0·1M-Benzenesulphonic acid	—	—	—	—	—	—	—	—
0·1M-Benzoquinone	—	—	—	—	—	—	—	—
0·1M-Phenol	—	—	—	—	—	—	—	—
0·1M-Pyridine	—	—	—	—	—	—	—	—
0·1M-Quinol	30	44	27	0·5	42	64	45	0·56
Group III								
0·01M-Acid magenta	—	—	—	—	77	70	95	1·0
0·00025M-Pinacyanol	32	44	28	0·45	60	87	55	0·75
0·025M-2 : 2′-Dipyridyl	36	68	28	0·9	48	—	—	—
0·01M-Sulphato-ester dye	—	—	—	—	65	90	55	1·4
0·01M-Anthraquinone-2-sulphonic acid	—	—	—	—	40	54	35	0·54
Dispersol fast crimson B (mixed film)	—	—	—	—	37	60	34	0·4

* The three figures under *a* show, in order: Molecular area (Å²) at zero compression, at commencement of development of measurable surface pressure, and at lowest point of upper linear part of force–area curve.

† Film compressibility, *b*, is expressed as slope of upper section of force–area curve (units: Å²/dynes/cm.).

should have almost identical non-polar attraction, but different polar attraction for solutes introduced into the water phase, and any differences between their films in penetrability or expansion by the solute will thus be attributable to differences in the polar attraction of the keto- and the acetyl group. Polar attaction by the keto-group is in fact likely to be

very low, because ketones do not appear to form hydrogen-bond complexes with other solutes in water,[3] whereas acetates do.[4]

The solutes used are water-soluble compounds of varied molecular sizes and shapes.

FIG. 1. FIG. 2. FIG. 3.

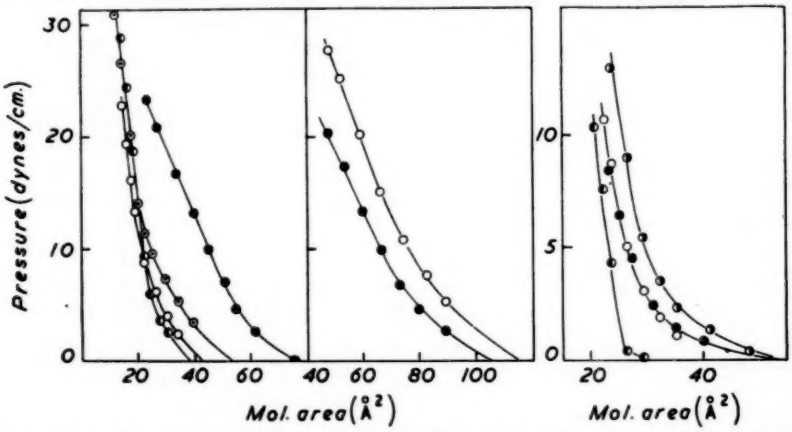


FIG. 1. *Cetyl acetate on various substrates*: ○, 0·1M-Sucrose; ◐, 0·1M-pyridine; ◌, 0·1M-benzoquinone; ●, 0·1M-quinol.

FIG. 2. *Cetyl acetate on dye solutions*: ○, 0·01M-Acid magenta; ●, 0·00025M-pinacyanol.

FIG. 3. *Ethyl stearyl ketone on various substrates*: ◐, Water; ●, 0·1M-quinol; ◑, 0·002M-pinacyanol; ○, 4·5M-urea.

FIG. 4. FIG. 5.

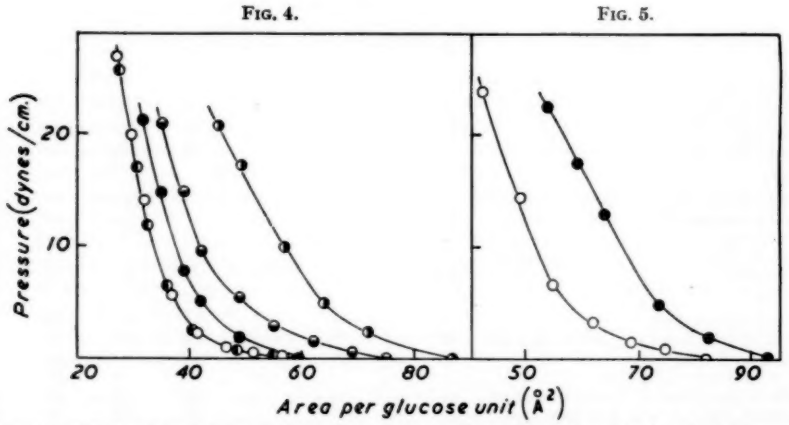


FIG. 4. *Cellulose triacetate on various substrates*: ○, Water; ●, 0·1M-quinol; ◑, 4·5M-urea; ◒, 0·025M-2 : 2′-dipyridyl; ◐, dispersol fast crimson B (mixed film).

FIG. 5. *Cellulose triacetate on various substrates*: ○, 0·0002M-Pinacyanol; ●, 0·01M-acid magenta.

The results are summarised in Tables 1 and 2 and in the Figures. The normal molecular area and compressibility data are given, together with other parameters sufficient to characterise the curves (Tables 1 and 2).

[3] Arshid, Giles, and Jain, *J.*, 1956, 559.
[4] *Idem*, *J.*, 1956, 1272.

TABLE 2. *Molecular areas, compressibilities, etc., of monolayers on tannic acid solutions*

Substrate	Cellulose triacetate				Cetylaniline			
	a *			*b* †	*a*			*b*
Water	45	61	42	0·5	25	32	25	0·6
Tannic acid	45	60	42	0·6	29	(37)	26	0·3
Concn. of tannic acid (mg./l.)	15				44			

Substrate	Cetyl acetate				*N*-Methylstearamide				Stearyl alcohol			
	a			*b*	*a*			*b*	*a*			*b*
Water	23	40	21	0·4	27	38	24	0·3	22	23	20	0·01
Tannic acid	28	(100)	24	0·7	31	65	24	0·4	26	31	25	0·4
Concn. of tannic acid (mg./l.)	44				46				46			

* † See footnotes, Table I.

RESULTS AND DISCUSSION

The solutes are conveniently classified according to the size of the hydrophobic residue in their molecules, and accordingly the results may be interpreted as follows:

Solutes with small molecules. There can be little non-polar attraction of these molecules, for the monolayers and their expansion effects must be almost entirely due to hydrogen-bond cross-linking. The ketone films are almost unaffected by them but both acetate films are expanded, so that the prediction of higher polar attraction in water by the acetate group than by the keto-group is confirmed.

The increase in both molecular area and compressibility of the acetate films on urea is particularly marked. Smaller effects are observed with ethylene glycol and mesaconic acid than with urea, which may be due to their small molecular size, allowing them to penetrate the film without much disturbance of packing. Neither, *e.g.*, high water solubility nor association in solution could account for the small effect of mesaconic acid: its solubility in water is only 2·7 g./100 c.c. at 18° (cf. phenol: 6·7 g./100 c.c. at 16°) and a determination of molecular weight showed that it is not associated in water; it should thus be free to form intermolecular bonds. Adsorption tests showed that ethylene glycol in aqueous solution appears to have no affinity for powdered cellulose triacetate.

On water, cellulose triacetate polymer chains are incompletely separated and do not form a true monolayer; *e.g.*, the apparent area per glucosidic residue, 37 Å^2, is only about half the theoretical value.[5] The chains are probably present as micellar bundles, but these are disaggregated by powerful hydrogen-bonding agents, *e.g.*, urea. (There must, of course, be a considerable attraction for water itself to enable the films to spread on water.)

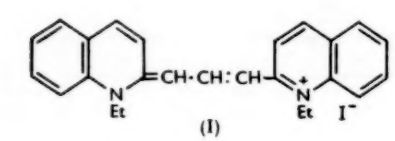
Solutes with medium-sized molecules. Phenol and quinol have considerable effect on acetate films, presumably by hydrogen bonding with the head groups therein; quinol no doubt acts as a cross-linking agent, as it does for some films of azo-compounds.[1] Phenol appears to raise the solubility of the film considerably, since the large effect on the compressibility and the magnitude of the increase in area are much more than can be accounted for by 1 : 1-attachment to the acetate groups in a rigid monolayer.

The small effects of benzenesulphonic acid, benzoquinone, pyridine, and sucrose are due to weak hydrogen-bonding power; and the very small effect on the cellulose triacetate film produced by ethyl methyl ketone, which is regarded as non-hydrogen bonding in water, shows that the triacetate has little ability to adsorb water-soluble solutes by other than hydrogen-bond forces.

Solutes with large molecules. The annexed dyes were amongst the compounds used. The ionic compounds expand the ketone films, presumably by non-polar association

[5] Borgin and Johnston, *Trans. Faraday Soc.*, 1953, **49**, 956.

between their hydrophobic residues and the alkyl chains of the ketone. Cetyl acetate, however, is affected considerably more than the ketones, clearly by a combination of polar and non-polar forces. The triacetate film is less expanded by the solutes with large molecules than is the cetyl acetate film, because of its smaller proportion of hydrophobic residue, and a comparison of effects produced by these solutes upon the several films shows that non-polar association probably plays little part in adsorption at the triacetate film.



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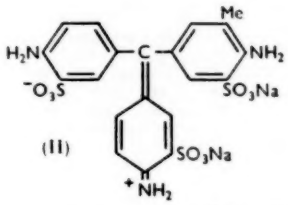

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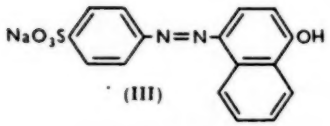

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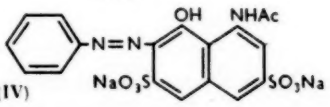

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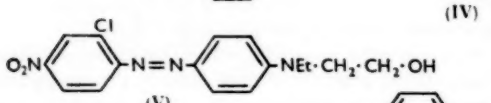

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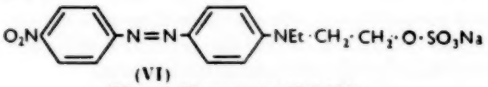

(VI)

(I) Pinacyanol (C.I.808).
(II) Acid magenta (C.I.692).
(III) Orange I (C.I.150).
(IV) Azo-geranine 2G (C.I.31).
(V) Dipersol fast crimson B (I.C.I.) (disperse dye for cellulose acetate, low water solubility; spread as a mixed film with cellulose triacetate).
(VI) Sulphato-ester dye (water-soluble dye for cellulose acetate).

The non-ionic disperse dye, which has a high affinity for cellulose acetate in bulk, when spread as a mixed film with cellulose triacetate produces no noticeable effect on the area or compressibility. Presumably it is adsorbed beneath the film, with its aromatic nuclei lying horizontally, in juxtaposition with the glucosidic rings.* Harding and Adam [6] noticed that the surface pressure of cellulose triacetate films on water is not appreciably altered by picric acid in the aqueous layer, but the surface potential is markedly lowered. They believed that the acid or its anion is adsorbed below the film.

Action of Tannic Acid.—Solutions of tannic acid were examined as substrates because the hydrogen-bonding properties of this compound with surface films have been the subject of thorough study by other authors by various means (see, *e.g.*, ref. 7). Protein films are made less compressible by tannic acid, which is adsorbed beneath the film and condenses together a number of protein chain molecules in a horizontal raft-like structure.[7] The present results (Table 2 and Fig. 6) demonstrate a somewhat different effect. The films of the monomeric compounds are slightly expanded at high pressures by tannic acid, and very considerably expanded at low pressures; they are made considerably more compressible in all cases except cetylaniline. It is suggested that at low pressures gaseous films of the hydrogen-bond complex of tannic acid with film monomer are formed, but with increasing pressure the film molecules tend to condense into the orientation normally

* The dye alone forms a condensed film on water with a molecular area of *ca.* 34 Å², which agrees closely with the value (32 Å²) estimated from models for vertical orientation on the OH group. Pressure steadily falls owing to the slow dissolution of the dye in water.

[6] Harding and Adam, *Trans. Faraday Soc.*, 1933, **29**, 837.
[7] Ellis and Pankhurst, *Discuss. Faraday Soc.*, 1954, **16**, 170.

taken up on water alone, with the tannic acid molecules bonded beneath the film. Thus the upper part of the π–A curves for films on water or tannic acid solution tend to coincide, showing that the acid has then become entirely forced out from the film into the underlying solution.

The film of cetylaniline is made *less* compressible by tannic acid, perhaps because of some form of association between the aromatic nuclei of the film and of the solute.

Cellulose triacetate on tannic acid behaves rather like the monomeric aliphatic compounds, but only if urea is also present in the solution, whereby its micelles are broken up; otherwise there is actually no significant effect on the film. Presumably, in this case the

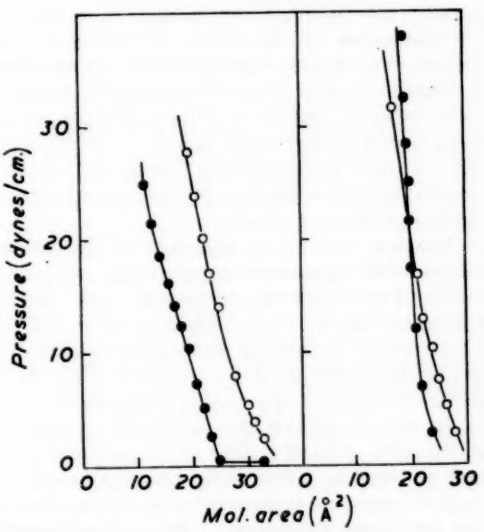

FIG. 6.

(Left) *Cetylaniline films on*: ●, Water; ○, tannic acid (44 mg./l.).

(Right) *Stearyl* (n-*octadecyl*) *alcohol films on*: ●, Water; ○, tannic acid (44 mg./l.)

tannic acid molecules are attached entirely beneath the cellulose triacetate micelles and, being much smaller than the latter, do not interfere with their compression or orientation.

Action of Non-ionic and Ionic Dyes upon Monolayers.—The above results show that a solute with a planar molecule and multiple points of attachment for hydrogen bonds around its periphery, as tannic acid has, does not necessarily cause much change in the area or compressibility of films of aliphatic compounds, including acetates, even though it is capable of forming bonds with the film molecules. Therefore the insignificant change in cellulose triacetate films when the highly substantive disperse dye is added is not inconsistent with a dye–acetate hydrogen-bonded attachment. The presence of sulphate ester, sulphonate, or other ionic groups in the dye, however, appears to prevent this " raft " type of attachment of dye beneath cellulose acetate, and considerable expansion occurs. This must be due to the effect of solvated water around the ionic groups, which prevents the necessary close approach of the two reacting molecules over their whole areas. Instead, the solute molecules penetrate the film *between* the individual chains in such a manner that individual acetate groups can become attached to hydrogen-bonding centres in the solute molecule and the ionic groups remain in the water below. This hypothesis helps to explain some of the phenomena of adsorption by cellulose acetates, as described below.

Adsorption Properties of Cellulose Acetates.—The adsorption properties of cellulose acetates for aromatic substances in aqueous solutions may briefly be described as follows:

(i) Most non-ionic polar compounds, *e.g.*, phenols and " disperse " dyes, are readily adsorbed by secondary cellulose acetate or cellulose triacetate. Exceptions to this rule

are very water-soluble substances with rather weak hydrogen-bonding groups, *e.g.*, aliphatic alcohols and pyridine. The disperse dyes are mostly azo- or anthraquinone derivatives containing a number of polar groups, *e.g.*, OH, NH_2, etc., but no ionic groups. Though they are almost insoluble in water, dyeing takes place through their extremely weak saturated solutions diffusing into the body of the polymer.[8,9]

(ii) The presence of any ionisable group in a dye almost entirely removes its affinity for cellulose triacetate, but not necessarily for the secondary acetate. Thus dyes with the sulphate ester group have high affinity for the latter. Even the highly ionised sulphonate group does not entirely destroy affinity for secondary acetate for this adsorbs monosulphonated dyes appreciably, but not disulphonated ones. Probably similar rules apply to the cationic groups in basic dyes, but information is not available on this point.

*Mechanism of Adsorption by Cellulose Acetates.**—Tests by the refractive-index method [10] (with some confirmation by infrared spectrophotometry [4,11]) used with solutions of binary mixtures of model compounds indicate that hydroxy-groups in dyes are bonded to the ether-oxygen atom of the acetate group in cellulose acetates,[10] and nitrogen atoms in dyes, to the methyl group, which is activated by the adjacent carbonyl double bond.[4,11] Both of these bonds are weak (except with powerful hydrogen-bonding agents, *e.g.*, phenol or urea) and the adsorption phenomena described above may be explained as follows in the light of the present results.

Cellulose acetates are hydrophobic and are little swollen in water. Any water-soluble solutes with hydrogen-bonding groups will penetrate into the amorphous, water-swollen region of the triacetate polymer in bulk and be adsorbed by hydrogen bonds, but the amorphous region is a very small proportion of the whole. Ionic dyes do this, but they do not penetrate the regions inaccessible to water; consequently their total adsorption is not practically significant (the adsorption of, *e.g.*, sulphato-ester dyes can readily be measured, though they do not appreciably colour the substrate).

In order to register any significant amount of adsorption a solute must penetrate some of the more ordered regions of the polymer not normally swollen by water. To do this each penetrating solute molecule must break simultaneously several interchain acetate–acetate bonds and replace them by dye–acetate bonds (hydrogen bonds and perhaps some van der Waals association). This it can probably do only if its own bonding groups are in at least two fairly widely spaced positions in the molecule, and no ionic groups are present to interfere in the manner referred to above. The penetration in this way of regions not normally swollen by water has some resemblance to solid solution, which for long was regarded as the mechanism of adsorption by cellulose acetate.[9]

The less highly ordered secondary acetate is more readily penetrated, and ionic compounds are as stated in many cases significantly adsorbed.

Experimental

Apparatus.—The unimolecular film balance used is a modification of Allan and Alexander's recent design.[12] The float is made of Duralumin, and the head is of brass and is pivoted on agate knife edges and planes; this allows it to be removed more readily than when spring-control is used. Allan and Alexander's instrument was designed for use at much lower surface pressures than those employed here, and the sensitivity of the present apparatus was accordingly reduced (to 0·1 dyne per cm.) by the use of a heavier beam. The ends of the beam were sealed to the trough by fine Polythene monofilament (0·005 in. Courlene X3, Courtaulds Ltd.).

The trough itself (10 × 25 cm. internal dimensions) was constructed from a single block of

* For summaries of hypotheses of the nature of the cellulose acetate–dye bond, see refs. 4, 9, and 11.

[8] Bird, Manchester, and Harris, *Discuss. Faraday Soc.*, 1954, **16**, 85.

[9] Vickerstaff, "The Physical Chemistry of Dyeing," Oliver and Boyd, Ltd., Edinburgh, 2nd edn., 1954.

[10] Arshid, Giles, McLure, Ogilvie, and Rose, *J.*, 1955, 67.

[11] Campbell, Cathcart, and Giles, unpublished work.

[12] Allan and Alexander, *Trans. Faraday Soc.*, 1954, **50**, 863.

Polythene, bolted to a brass plate for rigidity, and the movable barrier was also made of Polythene. This material has proved rather more convenient in use than glass, because the need for constant waxing of the surface is avoided except with some solutions of particularly low surface tension. The whole instrument is screened by an aluminium case, the barriers being mechanically controlled from outside. All measurements were made at room temperature. The ends of the bolts within the trough were wax coated.

Reagents.—Methyl stearyl ketone. Agaric acid (10 g.) and sulphuric acid (*d* 1·84) (100 c.c.) were heated on a water-bath for 1 hr., then cooled in ice, and mixed with 2 l. of water, and the mixture was extracted with ether. The ether extract was shaken with aqueous potassium carbonate solution, then filtered, and the ether removed. The residue was dissolved in ethanol, decolorised by charcoal, and recrystallised several times from ethanol, forming colourless plates, m. p. 56°.

Ethyl stearyl ketone. This was prepared by Gilman and Nelson's method.[13] Powdered cadmium chloride (0·16 mole) was stirred gradually into an ice-cooled ether solution of methylmagnesium bromide [prepared from magnesium (0·35 mole) and ethyl bromide (0·3 mole)] and stirring was continued for 30 min. Stearoyl chloride was then added gradually, at first in ether (0·05 mole in 40 c.c.) and then undiluted (0·16 mole). Stirring was continued for 1 hr. in the cold and then for 2 hr. on the boiling-water bath. Crushed ice was then carefully added, followed by water and sufficient sulphuric acid to dissolve the white precipitate formed. The ether layer was washed with alkali and then with water and evaporated. The white solid residue was heated with concentrated aqueous sodium hydroxide solution, cooled, and separated by filtration; it was finally redissolved in ether, which was washed with water. The residue after evaporation of the ether was recrystallised twice from ethanol; it had m. p. 53°.

The preparation of cetyl acetate has already been described.[1] The samples of cellulose triacetate used for the experiments summarised in Table 4 (and Figs. 4 and 5) and Table 2 had Ac, 58 and 62·5%, respectively. Both were spread from chloroform solution. The other reagents were pure laboratory or commercial products; distilled water was used for the aqueous phase. The sulphonated dyes were recrystallised from water to 91—98% purity ($TiCl_3$ analysis): remaining impurites are likely to be sodium chloride or bound water.

Solute Concentration.—As in the previous work, the solutes were used mostly at the highest practicable concentration, in aqueous solution, in some cases approaching saturation. It seems likely that under these conditions a very high proportion of active monolayer head-groups will be attached by polar bonds to solute molecules. Tests made with cetyl acetate films on phenol solutions of increasing concentration show that above 0·05M no further film expansion occurs with increase in solute concentration.

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[13] Gilman and Nelson, *Rec. Trav. chim.*, 1936, **55**, 518.

XUM

865. *Stages in Oxidations of Organic Compounds by Potassium Permanganate. Part VIII.* The Mechanism of Oxidation of Acraldehyde by Manganic Pyrophosphate.*

By Haring Land and William A. Waters.

The initial, rate-determining, stage in the oxidation of acraldehyde by manganic pyrophosphate is acid-catalysed and does not involve oxidant. It is suggested that this is the formation of the enol of β-hydroxypropionaldehyde:

$$H_2O + CH_2{:}CH{\cdot}CHO \xrightarrow{H^+} HO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OH$$

The faster oxidation of crotonaldehyde and the slower oxidation of α-methylacraldehyde appear to take a similar course, though with crotonaldehyde the oxidation step is rate-determining at low concentrations of the oxidant. The first oxidation product of acraldehyde appears to be glyceraldehyde and later a chelated manganic complex of glyceric acid seems to be formed. Further oxidative degradation occurs by glycol fission, formaldehyde and carbon dioxide being the eventual products, 10 equivalents of Mn^{III} in all being consumed.

In Part II [1] it was shown that the oxidations of propionaldehyde and *n*-butyraldehyde by manganic pyrophosphate occurred at rates which were of zero order with respect to tervalent manganese, and first order with respect to both aldehyde and hydrogen-ion concentrations, and continued far beyond the stage of oxidation of the aldehyde to the corresponding acid. It was suggested therefore that the one-electron oxidation followed rapidly upon a rate-controlling acid-catalysed enolisation. The study (Part VI [2]) of the oxidations of *cyclo*hexanone and of diethyl ketone supported this mechanism, for again oxidation followed an acid-catalysed enolisation and from *cyclo*hexanone the successive formation of 2-hydroxy-*cyclo*hexanone and then of *cyclo*hexane-1 : 2-dione was established. Related investigations of oxidations of aldehydes and ketones by alkaline ferricyanide [3] and by the free radical $\cdot ON(SO_3K)_2$ [4] supported the conclusion that oxidations of aldehydes and ketones by one-electron-abstracting reagents require the prior formation of an anion, $R'{\cdot}CH{:}CR{\cdot}O^-$, from which the removal of an electron is easy because it leads to production of a resonance-stabilised radical, $R'{\cdot}CH{:}CR{\cdot}O\bullet \longrightarrow R'{\cdot}\dot{C}H{\cdot}CR{:}O$. Removal of more electrons from this radical then occurs at the α-carbon atom so that α-hydroxy-aldehydes or -ketones are the primary products.

We have extended this work to the oxidation by manganic pyrophosphate of the αβ-unsaturated aldehyde acraldehyde, with which enolisation to give hydroxyallene, $CH_2{:}CH{\cdot}CHO \rightleftharpoons CH_2{:}C{:}CH{\cdot}OH$, must be regarded as very improbable, and in the course of the investigation we have made a more cursory examination of the corresponding oxidations of crotonaldehyde and α-methylacraldehyde. The latter compound cannot enolise by ionisation of an α-hydrogen atom yet all three aldehydes are easily oxidised.

Though manganic pyrophosphate does not attack olefinic double bonds, as in acrylic and crotonic acids, iodometric estimation of tervalent manganese during the oxidations of the unsaturated aldehydes was vitiated by the rapidity of addition of iodine to the olefinic groups. Fortunately, however, secondary reactions due to atmospheric oxygen, as encountered in several other cases with tervalent manganese,[2,5] were not significant

* Part VII, *J.*, 1956, 717.

[1] Drummond and Waters, *J.*, 1953, 440.
[2] Drummond and Waters, *J.*, 1955, 497.
[3] Speakman and Waters, *J.*, 1955, 40.
[4] Allen and Waters, *J.*, 1956, 1132.
[5] Drummond and Waters, *J.*, 1954, 2456.

enough to cause difficulty in spectrographic measurements with a Hilger "Spekker" photo-absorptiometer and the reactions were sufficiently fast to allow of simple but adequate temperature control.

Initial Stage of the Oxidation.—Table 1 shows that the oxidation of acraldehyde is a first-order reaction with respect to aldehyde, and Tables 2 and 3 show that the rate is of

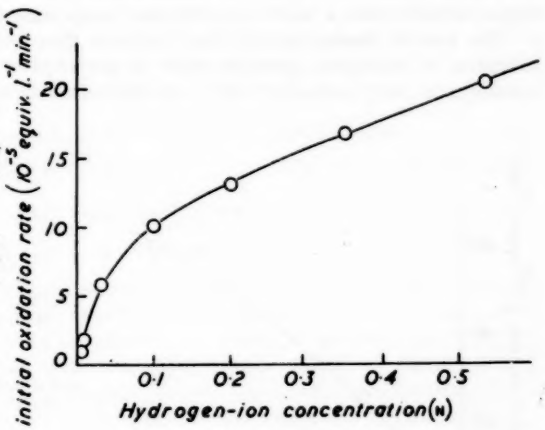


FIG. 1. *Initial rate of oxidation of acraldehyde by manganic pyrophosphate at various acidities.*

Initial [Acraldehyde], $9{\cdot}0 \times 10^{-3}$M; initial [Mn^{III}], $2{\cdot}32 \times 10^{-3}$M; total pyrophosphate, 0·050M; temp. 17·5° ± 0·1°.

zero order with respect to tervalent manganese except at very low concentrations of the oxidant. Fig. 1 shows that, in solutions of sufficient acidity for the successive ionisation

TABLE 1. *Dependence of rate on initial acraldehyde concentration.*

Initial [Mn^{III}], $7{\cdot}60 \times 10^{-3}$M; total pyrophosphate, $4{\cdot}54 \times 10^{-3}$M; pH, 1·20

Initial [Acraldehyde] ($\times 10^{-2}$M)	6·53	5·44	3·81	2·72	2·04	1·36	0·68
Initial rate, $-d[Mn^{III}]/dt$ ($\times 10^{-4}$ mole $l.^{-1}$ $min.^{-1}$)	6·3	4·9	3·5	2·5	1·8	1·2	0·7
Rate/[Acraldehyde]	0·96	0·90	0·92	0·92	0·88	0·88	1·03

TABLE 2. *Rate of consumption of* Mn^{III}

Initial [Acraldehyde], $2{\cdot}72 \times 10^{-2}$M; initial [$Mn^{III}$], $7{\cdot}60 \times 10^{-3}$M; total pyrophosphate $4{\cdot}54 \times 10^{-2}$M; pH, 1·20

Time (min.)	2	3	4	5	6	7	8	9	10	11
[Mn^{III}] (10^{-3}M)	7·18	6·90	6·60	6·32	6·08	5·82	5·57	5·32	5·07	4·57
$\Delta[Mn^{III}]$ Δt	0·21	0·23	0·25	0·25	0·25	0·25	0·25	0·25	0·25	0·25

TABLE 3. *Dependence of initial rate on* [Mn^{III}].

Total pyrophosphate, 0·150M; pH, 1·62

	(*A*) Initial [Acraldehyde], $3{\cdot}14 \times 10^{-2}$M.				(*B*) Initial [Acraldehyde], $9{\cdot}0 \times 10^{-2}$M.				
Initial [Mn^{III}] (10^{-3}M)	27·9	18·6	9·3	7·0	4·6	2·3	1·7	1·2	0·6
Initial rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)	13	13	13	12	13	3·4	3·4	3·2	3·0
Initial rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$) calc. for acraldehyde (*A*)					12	12	11	10	—

of the complex, $Mn(H_3P_2O_7)_3$, to be insignificant,[6] the reaction shows a first-order hydrogen-ion catalysis. Table 4 shows that the initial rate of oxidation is not affected by production of manganous ions. In all these kinetic features the oxidation of acraldehyde resembles that of propionaldehyde. In Tables 1—4 the temperature is 17·5°.

Comparative experiments with crotonaldehyde and with α-methylacraldehyde indicate that the former is oxidised somewhat more rapidly, and the latter much more

[6] Kolthoff and Watters, *J. Amer. Chem. Soc.*, 1948, **70**, 2455.

slowly, than is acraldehyde, both oxidations being substantially of first order with respect to aldehyde concentration (Table 5). Over the concentration and acidity range chosen for all these measurements the initial rate of oxidation of crotonaldehyde is still dependent upon manganic salt concentration (Fig. 2) though there is an evident trend towards a limiting zero-order rate at high manganic concentration. With α-methylacraldehyde the zero-order rate with respect to oxidant has again been found, though further critical testing of this over a wide concentration range may be of interest.

The kinetic measurements thus indicate that with each aldehyde the one-electron oxidation by manganic pyrophosphate is preceded by an acid-catalysed reaction. With acraldehyde, and probably with α-methylacraldehyde, the actual oxidation step is so

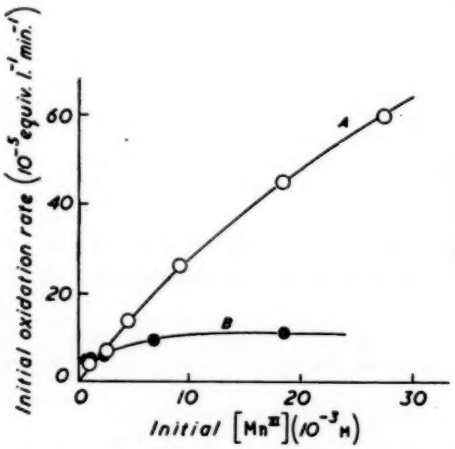


FIG. 2. *Initial rates of oxidation of crotonaldehyde and of α-methylacraldehyde.*

A, Initial [Crotonaldehyde], $9{\cdot}68 \times 10^{-3}$M; *B*, initial [α-Methylacraldehyde], $2{\cdot}22 \times 10^{-3}$M; temp., 17·5°; pH, 1·00; total pyrophosphate, 0·150M.

fast that the acid-catalysed reaction is rate-controlling: with crotonaldehyde this initial process is apparently rapid enough to make the oxidation step the rate-controlling one unless high concentrations of manganic salt are used. In the presence of vinyl cyanide the oxidation of acraldehyde by manganic pyrophosphate induced the separation of a

TABLE 4. *Oxidation in presence of manganous ions.*

Initial $[Mn^{III}]$, $1{\cdot}16 \times 10^{-3}$M; initial [Acraldehyde], $1{\cdot}07 \times 10^{-3}$M; total pyrophosphate, 0·042M; pH, 1·67

[The ionic strength of the solution was kept constant by replacing $MnSO_4$ with the requisite amount of $(NH_4)_2SO_4$.]

$[MnSO_4]$ (10^{-3}M)	0·0	30·1	51·6	258
Initial rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)	4·9	4·7	4·6	4·7

TABLE 5. *Oxidations of crotonaldehyde and of α-methylacraldehyde at* 17·5°: *dependence of initial rate on aldehyde concentration.*

Initial $[Mn^{III}]$, $4{\cdot}64 \times 10^{-3}$M; pyrophosphate, 0·050M; pH, 1·10

Crotonaldehyde oxidation			α-Methylacraldehyde oxidation		
Initial [Aldehyde] (10^{-3}M)	Initial rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)	Rate − 3·3 / [Aldehyde]	Initial [Aldehyde] (10^{-3}M)	Initial rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)	Rate / [Aldehyde]
77	85	1·06	90	14·5	0·16
52	59	1·07	60	9·6	0·16
26	32·4	1·12	30	5·3	0·18
14	17·6	1·02	15·1	3·2	0·21
6·5	11·6	1·28	7·5	1·3	0·17
2·8	6·4	1·11			

polymer that had an infrared absorption indicating the presence of both OH and CO groups. This indicates that an active free radical had been formed from the acraldehyde. However, the formation of the polymer did not affect the rate of consumption of Mn^{III}. This is to be expected, since the oxidation process which yields the free radical is much faster than the rate-controlling initial reaction.

It is currently agreed that in all acid-catalysed reactions of aliphatic aldehydes and ketones the actual process of proton addition to the oxygen atom of a carbonyl group is an instantaneous equilibrium and that the rate-controlling step is the following slow addition of an anion to this primary cation from a solvent molecule such as water. In the case of acraldehyde the initially formed cation is a mesomeric system:

$$CH_2{:}CH{\cdot}CHO + H^+ \rightleftharpoons CH_2{:}CH{\cdot}\overset{+}{C}H{\cdot}OH \longleftrightarrow \overset{+}{C}H_2{\cdot}CH{:}CH{\cdot}OH$$

so that, in water, the formation of two isomeric hydrates of acraldehyde can be envisaged:

$$CH_2{:}CH{\cdot}\overset{+}{C}H{\cdot}OH + H_2O \longrightarrow CH_2{:}CH{\cdot}CH(OH)_2 \qquad (I)$$

$$\overset{+}{C}H_2{\cdot}CH{:}CH{\cdot}OH + H_2O \longrightarrow HO{\cdot}CH_2{\cdot}CH{:}CH{\cdot}OH \qquad (II)$$

Studies of the rates of hydration of saturated aldehydes [7,8] have shown that the velocity of hydration of an aldehyde to products structurally resembling (I) is very much more rapid than the enolisation velocity as indicated by studies of one-electron oxidations, and hence oxidation of acraldehyde *via* compound (I) is unlikely. Again, chloral hydrate is not oxidised by manganic pyrophosphate.[1] Compound (II) however is the enol of β-hydroxypropionaldehyde; it could oxidise to the mesomeric radical, (III):

$$HO{\cdot}CH_2{\cdot}CH{:}CHO{\cdot} \longleftrightarrow HO{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CHO \qquad (III)$$

and thence to glyceraldehyde, $HO{\cdot}CH_2{\cdot}CH(OH){\cdot}CHO$, just as the enol of propionaldehyde would oxidise to α-hydroxypropionaldehyde. Consequently, we suggest that the formation of the enol (II) is the rate-determining step in the one-electron oxidation of acraldehyde. Similarly, α-methylacraldehyde can be envisaged as giving $HO{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}OH$, then $HO{\cdot}CH_2{\cdot}CMe(OH){\cdot}CHO$.

The acid-catalysed addition of water to acraldehyde has already been studied kinetically, first by Lucas and Pressman [9] and later by Hall and Stern.[10] These workers, however, have dealt with the reversible addition of a water molecule to the olefinic bond of acraldehyde to give the aldehydic form of β-hydroxypropionaldehyde and not the enol (II):

$$CH_2{:}CH{\cdot}CHO + H_2O \rightleftharpoons HO{\cdot}CH_2{\cdot}CH_2{\cdot}CHO$$

The earlier workers give the activation energy of the forward reaction as 18 kcal., whilst the later workers give 15·7 kcal. Both these values are much higher than the value of

TABLE 6. *Rates of oxidation of acraldehyde at different temperatures.*

Initial [Acraldehyde], 0·01M; total pyrophosphate, 0·125M; initial [Mn^{III}], $1{\cdot}55 \times 10^{-3}$M.

Temp.	44°	38°	32°	25°	17·5°
pH	1·05	1·00	1·02	1·04	1·05
Rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)	58	43	28	17	10
Rate corrected to pH 1·05	58	41	27	17	10

Activation energy (from graph): 12·9 ± 0·4 kcal.

12·9 ± 0·4 kcal. which we deduce from our oxidation-rate measurements over the temperature range 17·5—44° (Table 6) and undoubtedly we have not been concerned with this hydration of the olefinic bond. To confirm this we have demonstrated that if aqueous acraldehyde is left, under nitrogen, in contact with mineral acid for several hours before

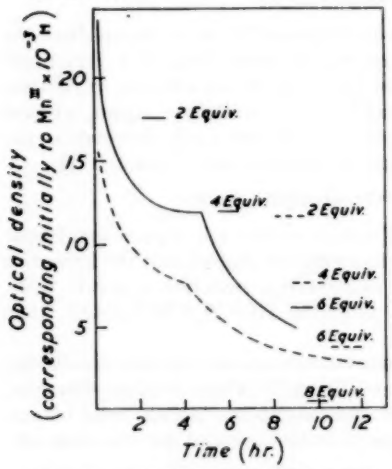
[7] Bell and Clunie, *Proc. Roy. Soc.*, 1952, *A*, **212**, 33.
[8] Bell and Darwent, *Trans. Faraday Soc.*, 1950, **46**, 34.
[9] Lucas and Pressmann, *J. Amer. Chem. Soc.*, 1942, **64**, 1953.
[10] Hall and Stern, *J.*, 1950, 490.

it is oxidised with manganic pyrophosphate then the initial rate of oxidation decreases considerably (Table 7). We infer that β-hydroxypropionaldehyde yields the enol (II) much less rapidly that does acraldehyde. α-Methylacraldehyde behaves similarly, though the effect of pre-treatment with acid is proportionally much less.

The relative reactivities of acraldehyde, crotonaldehyde, and α-methylacraldehyde are explicable if the preceding reaction mechanism is correct:

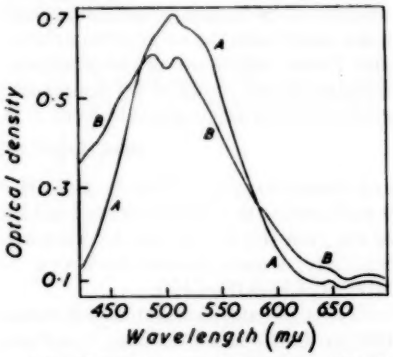
The inductive effect of a methyl group at an α-carbon atom would decrease the ease of catalysed hydroxylation at the double bond by compensating, in part, for the electro-

FIG. 3. *Complex formation in prolonged oxidation of acraldehyde with manganic pyrophosphate.*



Upper curve: Initial [Mn^{III}], $2{\cdot}33 \times 10^{-2}$M; [Acraldehyde], $5{\cdot}75 \times 10^{-3}$M.
Lower curve: Initial [Mn^{III}], $1{\cdot}55 \times 10^{-2}$M; [Acraldehyde], $3{\cdot}93 \times 10^{-3}$M.
Temp., 50°; pH, 0·12.

FIG. 4. *Absorptions of manganic complexes in a 1-cm. cell.*



(*A*) Manganic pyrophosphate; [Mn^{III}], $11{\cdot}5 \times 10^{-3}$M.
(*B*) Solution after oxidation of acraldehyde by 4 equiv. of Mn^{III} (Fig. 3, upper curve); residual [Mn^{III} *ca.* 8×10^{-3}M.

TABLE 7. *Effect of acid catalysis of hydration of acraldehyde on its rate of oxidation by* Mn^{III}.

(*A*) Initial [Mn^{III}], $2{\cdot}32 \times 10^{-3}$M; total pyrophosphate, 0·15M; pH, 1·66; temp., 17·5°; [Acraldehyde], $1{\cdot}38 \times 10^{-2}$M in oxygen-free distilled water. (Rates in 10^{-5} mole $l.^{-1}$ $min.^{-1}$.)

Initial rate, freshly prepared solution	4·7
Initial rate for solution stored for 18 hr. at room temp.	4·5

(*B*) The following solutions were stored in absence of oxygen for 24 hr. at 25°, then mixed with pyrophosphate, Mn^{III}, and sulphuric acid to give in each case [Acraldehyde], $1{\cdot}93 \times 10^{-2}$M; [$Mn^{III}$], $4{\cdot}64 \times 10^{-3}$M; pyrophosphate, 0·15M; pH, 1·65, and the rate of consumption of Mn^{III} was measured at 17·5°.

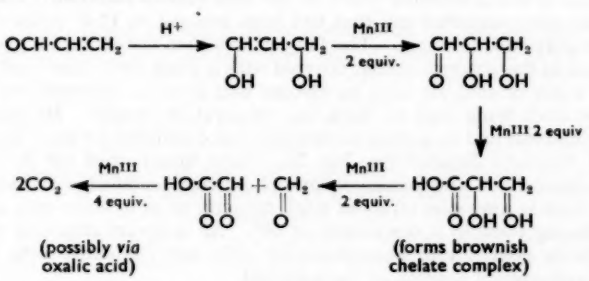
Solution	Oxidation rate (10^{-5} mole $l.^{-1}$ $min.^{-1}$)
(*a*) Acraldehyde in distilled water	7·8
(*b*) ,, 0·125M-pyrophosphate	4·4
(*c*) ,, 0·083M-pyrophosphate plus 0·57N-sulphuric acid	1·8
(*d*) ,, 0·85N-sulphuric acid	0·9

α-Methylacraldehyde (6×10^{-2}M), when stored as in (*a*) above, gave an initial rate of $9{\cdot}6 \times 10^{-5}$ mole $l.^{-1}$ $min.^{-1}$: after storage as in (*d*) the rate was $7{\cdot}9 \times 10^{-5}$ mole $l.^{-1}$ $min.^{-1}$.

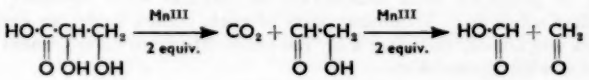
meric effect of the carbonyl group; in the β-position the methyl group would enhance this electromeric polarisation of the double bond.

Later Stages of the Oxidation.—To investigate the prolonged oxidation of acraldehyde, sealed ampoules containing oxygen-free solutions of acidified manganic pyrophosphate and acraldehyde were stored at 50° and after suitable intervals cooled to 10° and emptied into absorptiometer cells. Fig. 3 shows typical optical-density measurements made with a blue-green filter (No. 603). The discontinuities in the curves are due to the presence of a brownish-red intermediate having a broader absorption band than the cherry-red manganic pyrophosphate in the 450—600 mμ region (Fig. 4). This intermediate substance, which evidently reaches its maximum concentration when 4 equiv. of Mn^{III} have been consumed per mole of acraldehyde, is probably a chelated manganic complex of an α-hydroxy-acid, similar to those noted as being formed during the oxidations of lactic and tartaric acids.[11] Solutions containing as many as 6 equiv. of Mn^{III} were decolorised in a few days, one containing 8 equiv. became colourless in about a week, whilst one containing 10 equiv. remained slightly pink after 4 weeks. Titration of this solution indicated an overall consumption of 9·96 equiv. of Mn^{III} per mole of acraldehyde. A test with chromotropic acid showed that this final solution contained formaldehyde. Carbon dioxide was present but formic acid could not be detected. After consumption of 2 equiv. of Mn^{III} formaldehyde could not be detected in the solution; after consumption of 6 or more equiv. however it was present. At no stage was it possible to detect 1 : 2-dioxo-compounds, R·CO·CO·R′, by treating solutions with hydroxylamine and then with a nickel salt. Hence oxidation *via* $HO{\cdot}CH_2{\cdot}CO{\cdot}CHO$ is unlikely.

The evidence presented above indicates that the course of oxidation of acraldehyde can probably be represented as follows:



According to this scheme, glyceraldehyde yields glyceric acid which is then oxidised as a 1 : 2-glycol,[12] giving formaldehyde when 6 equiv. of Mn^{III} have been consumed. The glyoxylic acid must oxidise completely, *via* oxalic acid, and not undergo fission to formic acid since this is resistant to manganic pyrophosphate.[1] An alternative path from glyceric acid would be that suggested for α-hydroxy-acids in Part V,[11] but this is much less likely because it should end with the consumption of only 8 equiv. of tervalent manganese and should yield a mixture of formaldehyde and formic acid:



Further evidence that the oxidation of acraldehyde involves the successive formation of glyceraldehyde and of glyceric acid has been obtained by oxidising it with known amounts of manganic pyrophosphate and, when destruction of Mn^{III} was complete, adding standard periodate solution and estimating the further oxidation effected thereby

[11] Levesley and Waters, *J.*, 1955, 217.
[12] Drummond and Waters, *J.*, 1953, 3119.

in 4 hr. at 6°. Table 8 shows that the periodate consumption, appreciable after oxidation by 2 equiv. of Mn^{III}, rises to a maximum at the 4 equiv. stage (that of production of glyceric acid) and has almost disappeared when 6 equiv. of Mn^{III} have been consumed. Since cold periodic acid rapidly oxidises both 1 : 2-glycols and glycollaldehyde,[13] but oxidises glyoxylic acid very slowly,[14] these observations favour the view that manganic pyrophosphate oxidises glyceric acid by glycol fission rather than by decarboxylation.

Experimental

Materials.—Acraldehyde was twice fractionated in oxygen-free nitrogen through a short Vigreux column, the middle fraction only being collected. Immediately after distillation, quantities of about 1 g. were sealed in thin-walled glass bulbs and weighed. Solutions were prepared by breaking bulbs in boiled-out distilled water in standard flasks and immediately making them up to volume. In this way polymerisation of the acraldehyde was avoided. Crotonaldehyde and α-methylacraldehyde were purified similarly, but some slight polymerisation of the latter could not be prevented.

Manganic pyrophosphate solutions were prepared as described in Part II.[1]

Procedure for Kinetic Measurements.—Analyses were carried out with a Hilger "Spekker" photoabsorptiometer using blue-green filter No. 603. With 4-cm. cells the calibration curve was nearly linear over the concentration range 4—7 × 10^{-3}M-Mn^{III}; higher concentrations were measured in 1-cm. cells. The colour change due to the transient product (Fig. 3) does not affect the accuracy of the initial rate measurements.

Standard solutions of the components were prepared in oxygen-free distilled water and brought to 17·5°. Aliquot parts were then mixed inside the thermostat in a flask that was being continually flushed with oxygen-free nitrogen; the acraldehyde solution was added last and the instant of half admixture taken as the zero time of reaction. The mixture was then poured into an absorptiometer cell that had been brought to 17·5° inside the thermostat and flushed thoroughly with nitrogen. The full cell was then closed with a glass plate to exclude air, transferred to the absorptiometer, covered with a black cloth, and kept at 17·5° ± 0·1° by a current of warm or cold air from an electric hair-dryer, a thermometer in a second water cell under the cloth being used to check the temperature control. Measurements were made at 1—2 min. intervals and no kinetic experiment was continued for more than 30 min.

Studies of Prolonged Reaction (see Fig. 3).—These were carried out by mixing oxygen-free solutions of acraldehyde and manganic pyrophosphate, acidified with sulphuric acid to pH 0·12, sealing them in ampoules of about 8 ml. capacity so as to leave only about 0·2 ml. of gas space, and placing these in a thermostat at 50°. At intervals ampoules were cooled to 10°, and the contents poured into absorptiometer cells and compared with a freshly-prepared manganic pyrophosphate solution at the same pH.

The data of Fig. 4 were obtained by rapid use of a Unicam spectrophotometer with a solution that showed maximum colour deviation.

Completion of reaction was tested by sealing similar ampoules of acraldehyde with 2, 4, 6, 8, and 10 equiv. of manganic pyrophosphate and storing them at 50°. Solutions containing up to 6 equiv. of Mn^{III} were decolorised completely in 1—2 days, that with 8 equiv. became colourless after a week, and that with 10 equiv. remained slightly pink after 4 weeks and had deposited a trace of manganese dioxide. Colour tests[15] for possible reaction products, *i.e.*, CH_2O, $H{\cdot}CO_2H$, $\cdot CO{\cdot}CO\cdot$, were made with each of these decolorised solutions.

Consumption of periodate after completion of reaction with tervalent manganese was examined in similar solutions. To aliquot parts of each, cooled to 6°, an excess of standard periodate solution was added, and after 4 hr. the iodine liberated on treatment with potassium iodide was titrated with thiosulphate.

Induced Polymerisation of Vinyl Cyanide.—This was examined in evacuated Thunberg tubes containing in each case 0·3 ml. of vinyl cyanide in 15 ml. of solution. A solution containing acraldehyde (0·03M) in acid pyrophosphate was not turbid after 18 hr., solutions containing acid manganic pyrophosphate (4 × 10^{-3}M) and neutral manganic pyrophosphate

[13] Fleury and Courtois, *Bull. Soc. chim. France*, 1941, **8**, 75; 1945, **12**, 548.
[14] Fleury and Lange, *J. Pharm. Chim.*, 1933, **17**, 196, 313, 409.
[15] F. Feigl, "Spot Tests," 4th English Edition, Elsevier Publ. Co., Amsterdam, 1954.

(4×10^{-3}M) plus acraldehyde (0·03M) contained only a minute amount of polymer after 18 hr., but a solution containing the same concentrations of acraldehyde and manganic pyrophosphate in approx. N-sulphuric acid gave an immediate separation of polymer. Decoloration of this

TABLE 8. *Formation of a* 1 : 2*-glycol by oxidation of acraldehyde with manganic pyrophosphate.*

Initial [Acraldehyde] (10^{-3}M)	Mn^{III} reduced (equiv.)	Periodate reduced (10^{-3}M)	Molar fraction of glycol present
1·21	2	0·145	0·12
0·97	4	0·355	0·37
0·85	6	0·024	0·03
0·79	8	nil	0·00

solution was complete in 9·60 min.; a similar solution not containing vinyl cyanide was decolorised in 9·67 min. The collected polymer had infrared absorption bands at 1720 (CO) and 3450 $cm.^{-1}$ (OH).

One of us (H. L.) thanks the British Council for a Scholarship.

THE DYSON PERRINS LABORATORY, OXFORD. [*Received, May 6th,* 1957.]

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866. *The Chemistry of Quadrivalent Germanium. Part V.* Ion-exchange Studies of Germanate Solutions containing Polyhydric Alcohols.*

By D. A. EVEREST and J. C. HARRISON.

Ion-exchange studies of solutions of germanates containing ethylene glycol, glycerol, and mannitol have been carried out over the pH range 6—12 with Amberlite I.R.A. 400-Cl. With ethylene glycol only chloride and germanate ions are taken up by the exchanger at all pH values. In presence of glycerol, chloride and germanate ions only are sorbed up to pH 9, whilst at higher pH values a doubly charged 1 : 1 monogermanic acid–glycerol complex is also sorbed. With solutions containing a germanium : mannitol mole ratio of 1 : 5 or 1 : 7 a singly charged 1 : 1 monogermanic acid–mannitol complex is taken up by the resin along with chloride up to pH 8. Above pH 10·6 a doubly charged 1 : 2 monogermanic acid–mannitol complex is sorbed together with chloride. A mixture of these ions is sorbed between pH 8 and 10·6. With solutions containing a germanium : mannitol mole ratio of 1 : 1 a singly charged monogermanic acid–mannitol complex is sorbed along with germanate and chloride at all pH values studied.

THE formation of complexes between germanic acid and polyhydric alcohols has often been observed.[1,2] Their formation enhances the solubility of germanium dioxide and the acid strength of germanic acid and allows the latter to be quantitatively titrated with alkali as if it were a strong monobasic acid. In absence of mannitol, and with phenolphthalein as indicator, the titration of germanic acid gives an end-point of 2 moles of sodium hydroxide to 5 g.-atoms of germanium, *i.e.*, corresponding to the titration of pentagermanic acid. The pH of the phenolphthalein end-point is close to 9·2, at which value ion-exchange [3,4] and other methods [5] indicate that the proportion of germanic acid

* Part IV, *J.*, 1957, 1820.

[1] Bardet and Tchakarian, *Compt. rend.*, 1928, **186**, 637; Tchakarian, *ibid.*, 1928, **187**, 229; Poluektov, *Mikrochemie*, 1935, **18**, 48; Cluley, *Analyst*, 1951, **76**, 517; Tchakarian, *Bull. Soc. chim. France*, 1943, **10**, 98.

[2] Tchakarian, *Ann. Chim.* (*France*), 1939, **12**, 415.

[3] Everest and Salmon, *J.*, 1954, 2438.

[4] *Idem*, *J.*, 1955, 1444.

[5] Lourijsen-Teyssedre, *Bull. Soc. chim. France*, 1955, 1118.

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in solution present as pentagermanic acid is then a maximum. Addition of mannitol (M) appears to degrade the pentagermanic acid to form a complex formulated by Tchakarian [2] as $H_2[Ge_2O_5(M_n)]$, where n must be at least two. The stability of these polyhydroxy-complexes of germanic acid appears to be considerable; no precipitate of germanium dioxide is obtained on addition of ammonia (cf. preparation of activated germanium dioxide [6]) or of magnesium germanate with magnesium chloride; the precipitation of magnesium germanate from germanate solutions is normally quantitative.[7]

Similar complex formation with polyhydroxy-compounds has been observed with other inorganic acids (*e.g.*, between mannitol and molybdic,[8] bismuthic,[9] arsenious,[10] telluric,[11,12] niobic,[13] tantalic,[14] and zirconic acid [15] and between glycerol and telluric acid [11,12] in addition to the well-known mannitol– and glycerol–boric acids). It is significant that most of the above acid readily undergo condensation reactions under the correct conditions. We therefore studied the reaction of germanic acid, whose condensation reactions are now fairly well known, with three typical polyhydroxy-compounds: ethylene glycol, glycerol, and mannitol, to gain information about the complexes formed and the effect of these polyhydroxy-compounds on the normal condensation reactions of germanic acid. The success of ion-exchange methods in studying other complex systems [3,4,16] led us to use similar methods.

Experimental

Equilibrium Experiments and Analytical Methods.—At least 14 days with frequent shaking was allowed for the establishment of equilibrium between the resin and solution. The solution was then decanted from the resin and the latter transferred to a short column and rapidly flushed with water to remove adhering solution. The resin was then eluted with 0·1N-sodium hydroxide (100 ml.) and 0·1N-sulphuric acid (100 ml.), both fractions being collected together. Germanium was determined iodometrically in an aliquot part of the eluate after reduction to the bivalent state with hypophosphorous acid [6] and chloride was determined gravimetrically as silver chloride. Polyhydric alcohols were determined by adding to an aliquot portion of the resin eluate (containing not more than 0·1 mmole of mannitol, 0·25 mmole of glycerol, or 0·5 mmole of ethylene glycol) 3N-hydrochloric acid (3 ml.) and 0·1N-potassium periodate (50 ml.). The mixture was kept for 30 min. at room temperature out of direct sunlight, solid potassium iodide (1 g.) was then added, and after 1—2 min. the liberated iodine was titrated with 0·1N-sodium thiosulphate. A blank experiment on the periodate solution was performed simultaneously.

Results

Ethylene Glycol–Germanate System.—In Table 1 are given the results for the sorption of germanium and chloride by Amberlite I.R.A. 400-Cl (0·25 g.) from solutions containing 2 mg.-atoms of germanium, 10 mmoles of ethylene glycol, and 0·75 mmole of chloride (as resin chloride) in 75 ml. of solution. The sorption of ethylene glycol by the resin was negligible at all pH values. The R values in Table 1 refer to the number of germanium atoms present in 1 equiv. of germanate ions sorbed by the resin; they were calculated as previously described.[3]

Glycerol–Germanate System.—Table 2 gives the results for the sorption of germanium, chloride, and glycerol by the resin (0·25 g.) from solutions containing 2 mg.-atoms of germanium, 10 mmoles of glycerol, and 0·75 mmole of chloride (as resin chloride) in 75 ml. of solution.

[6] Everest, *J.*, 1953, 4117.
[7] Muller, *J. Amer. Chem. Soc.*, 1922, **44**, 2439.
[8] Darmois, *Bull. Soc. chim. France*, 1928, **43**, 1214.
[9] Vanino and Hauser, *Z. anorg. Chem.*, 1901, **28**, 210.
[10] Auerbach, *ibid.*, 1903, **37**, 353.
[11] Rosenheim and Weinheimer, *ibid.*, 1911, **69**, 266; Roy, Lafferriere, and Edwards, *J. Inorg. Nuclear Chem.*, 1957, **4**, 106.
[12] Antikainen, *Suomen Chem.*, 1956, **29**, *B*, 135.
[13] Hauser and Herzfeld, *Zentr. Min.*, 1910, 758.
[14] Hauser, *Z. anorg. Chem.*, 1908, **60**, 230.
[15] Tchakarian, *Bull. Soc. chim. France*, 1932, 846.
[16] Everest, *J.*, 1955, 4415; Everest and Harrison, *J.*, 1957, 1439, 1820.

TABLE 1. *Sorption of germanium and of chloride from solutions (75 ml.) by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	*R*	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	*R*
3·95	—	1·0	—	9·8	1·53	0·35	2·35
6·1	0·67	0·76	2·8	10·1	1·32	0·37	2·1
6·95	1·23	0·56	2·8	10·85	0·56	0·50	1·1
8·2	1·79	0·365	2·8	11·4	0·33	0·46	0·61
8·8	1·88	0·32	2·75	12·05	0·28	0·43	0·49
9·5	1·78	0·32	2·6				

TABLE 2. *Sorption of germanium, chloride, and glycerol from solutions (75 ml.) by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Glycerol	Calc. capacity (equiv. per equiv. of resin)	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Glycerol	Calc. capacity (equiv. per equiv. of resin)
5·5	—	1·0	—	—	11·25	0·20	0·615	0·21	1·02
7·0	1·27	0·565	0·04	1·01 *	11·5	0·20	0·57	0·205	0·97
8·2	1·56	0·42	0·04	0·98 *	11·75	0·215	0·58	0·18	1·01
8·9	1·33	0·48	0·04	0·99 *	12·0	0·215	0·55	0·20	0·98
9·5	0·82	0·56	0·09	1·02	12·1	0·23	0·53	0·18	0·99
9·85	0·30	0·585	0·17	0·98	12·2	0·22	0·53	0·18	0·97
10·6	0·20	0·595	0·195	0·99	12·3	0·215	0·52	0·185	0·95

* Calculated on the assumption that only free germanate and chloride are sorbed by the resin.

Mannitol–Germanate System.—Results for the sorption of germanium, chloride, and mannitol by the resin from (*a*) 1 : 5 solutions, (*b*) 1 : 1-solutions and (*c*) 1 : 7 solutions are given in Table 3. For the 1 : 7 solution the sorption of chloride and germanium only was measured. In all cases the minimum of resin chloride was present, *ca.* 0·75 mmole.

TABLE 3. *Sorption of germanium, chloride, and mannitol from solutions (75 ml.) by Amberlite* I.R.A. 400-Cl (0·25 g.).

pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Mannitol	Calc. capacity (equiv. per equiv. of resin)	pH of soln.	Species sorbed (moles or g.-atoms per equiv. of resin) Ge	Cl	Mannitol	Calc. capacity (equiv. per equiv. of resin)
(*a*) 2 mg.-atoms of germanium and 10 mmoles of mannitol present (1 : 5).									
3·6	—	1·0	—	—	8·0	0·32	0·575	0·44	0·895 1·215 *
5·3	0·15	0·86	0·21	1·01	10·1	0·39	0·46	0·54	0·85 1·24 *
5·75	0·25	0·765	0·31	1·01	10·6	0·32	0·43	0·59	1·07 *
6·1	0·32	0·725	0·37	1·04	11·2	0·30	0·38	0·59	0·98 *
6·6	0·37	0·66	0·43	1·03	11·5	0·29	0·36	0·59	0·94 *
(*b*) 2 mg.-atoms of germanium and 2·0 mmoles of mannitol present (1 : 1).									
3·9	—	1·0	—	—	11·0	0·76	0·214	0·595	0·99
6·5	0·615	0·67	0·16	0·99	11·6	0·765	0·18	0·665	1·02
7·4	0·79	0·445	0·345	0·97	11·85	0·73	0·17	0·70	0·93
7·6	0·84	0·405	0·38	0·96	11·95	0·705	0·15	0·655	0·93
8·0	0·85	0·34	0·46	0·95	12·05	0·69	0·17	0·66	0·89
8·4	0·85	0·335	0·53	0·99	12·15	0·685	0·175	0·585	0·96
(*c*) 1·4 mg.-atoms of germanium and 10 mmoles of mannitol (1 : 7).									
5·0	0·115	0·91	—	1·02	6·0	0·255	0·77	—	1·02
5·4	0·16	0·85	—	1·01	6·3	0·34	0·73	—	1·07
5·7	0·20	0·79	—	0·99	6·8	0·28	0·74	—	1·02

* Sorption of a bivalent 1 : 2 monogermanic acid–mannitol complex postulated.

Discussion

Ethylene Glycol–Germanate System.—The results in Table 1, together with the fact that no ethylene glycol is taken up by the resin, indicate that only germanate and chloride are taken up. The R values calculated are consistent with the sorption of pentagermanate (R 2·5) at *ca.* pH 9, whilst an increasing proportion of the sorbed germanium is present as monogermanate ($HGeO_3^-$, R 1·0; or GeO_3^{2-}, R 0·5) at higher pH values owing to the depolymerisation of the pentagermanate ion: That R remains at a little above 2·5 when the pH falls below 9 is similar to the behaviour of germanate solutions with large amounts of chloride present.[3] These high R values may be due to the sorption of traces of a higher germanate polymer of greater R value, but they are more probably due to the sorption of small quantities of $HGe_5O_{11}^-$ (R 5·0) at these lower pH values. The presence of ethylene glycol appears to inhibit the sorption of monogermanate ions by the resin just as do chloride ions.[3] Monogermanate ions are taken up by the resin at these lower pH values in presence of small or zero amounts of chloride.[4]

Glycerol–Germanate System.—At pH 8·9 and below, the sorption of glycerol by the resin (Table 2) is only slightly greater than the trace quantity (*ca.* 0·02 mmole per equiv. of resin, cf. ref. 16) of glycerol physically entrained inside the resin. Between pH 7 and 8·9 the capacity of the resin can be reasonably accounted for in terms of the sorption of chloride and pentagermanate ions by the resin. Above pH 9 the sorption of glycerol by the resin increases whilst the sorption of germanium falls off relatively more quickly than in the ethylene glycol system (Table 1). This behaviour indicates that a germanium–glycerol complex is being taken up by the resin, and that formation of this complex increases the extent of depolymerisation of the pentagermanate ion. The capacity of the resin above the pH 9 can be accounted for to within 5% by assuming the sorption of a doubly charged 1 : 1 monogermanic acid–glycerol complex by the resin, together with chloride and free germanate. The R value of this free germanate (*i.e.*, the ratio of pentagermanate to monogermanate taken up by the resin) was taken from the values found in the ethylene glycol system (Table 1). The method of calculating the resin capacities from the experimental results followed the method previously described.[3,4,16]

Although addition of glycerol does not appear to affect the condensation of monogermanic acid below pH 8, it considerably reduces the degree of condensation at higher pH values by complexing with monogermanic acid. This is illustrated by the fact that the maximum sorption of germanium in presence of glycerol was 1·6 g.-atoms per equiv. of resin at pH 8·0. This is in contrast to the behaviour found in the ethylene glycol system where a maximum germanium sorption of 1·9 g.-atoms of germanium occurred at pH 9·2. The concentration of pentagermanate in solution and its sorption by the resin is normally a maximum at pH 9·2 in non-complex-forming systems.[3,4,5]

Our results are similar to Antikainen's for the telluric acid–glycerol system.[12] He showed from potentiometric and cryoscopic experiments that only a 1 : 1 complex was formed in this system, no higher complex being detected.

Mannitol–Germanate System.—In solutions containing a germanium : mannitol mole ratio of 1 : 7 or 1 : 5 (Table 3) the resin capacity below pH 8 can be satisfactorily accounted for in terms of the sorption of a singly charged 1 : 1 monogermanic acid–mannitol complex by the resin together with chloride, no free germanate being sorbed. These calculations were based on the germanium sorption figures rather than those of mannitol as the former were considered the more accurate. The mannitol figures confirm, however, that it is just a mixture of these two ions which is taken up by the resin. Above pH 10·6 the capacity of the resin can be quantitatively accounted for in terms of the sorption of a doubly charged 1 : 2 monogermanic acid–mannitol complex by the resin together with chloride, but again no free germanate. Between pH 8·0 and 10·6 a mixture of these two complexes is sorbed by the resin together with chloride. It is evident that in these 1 : 7 and 1 : 5 solutions the mannitol forms complexes so strongly with the monogermanic acid

that the normal condensation reactions of germanic acid are entirely repressed, and no free monogermanate or pentagermanate remains in solution.

Similar results have been observed in mannitol–boric acid solution.[17] Either a 1 : 1 or a 1 : 2 boric acid–mannitol complex is formed, depending upon the conditions.

In the solutions containing a germanium : mannitol mole ratio of 1 : 1 the resin capacity can be accounted for over the whole pH range by assuming a singly charged 1 : 1 monogermanic acid–mannitol complex to be sorbed by the resin together with chloride and free germanate. As before, R for the free germanate taken up by the resin was taken from those obtained in the ethylene glycol system (Table 1).

It is obvious from Table 3 that more germanium and mannitol are taken up by the resin from solutions with the lower mannitol concentration. This apparently anomalous behaviour can be explained if it is assumed that appreciable quantities of an uncharged germanium–mannitol complex are formed in solutions containing excess of mannitol. Formation of such a complex would decrease the effective concentration of available mannitol and germanium in solution and allow relatively more chloride to be taken up by the resin.

Mannitol evidently forms complexes more strongly with monogermanic acid than does glycerol, and ethylene glycol forms complexes extremely weakly. This is in the same general order as found in other systems (*e.g.*, ref. 18). These three polyhydric alcohols affect the condensation of germanic acid in a similar order—the stronger the complex formed the greater is the degree of suppression of the normal condensation process.

It is noteworthy that the rate of polymerisation of silicic acid above pH 8 is considerably reduced by addition of glycerol and other polyols.[19] This probably indicates that monosilicic acid forms complexes with them under similar conditions to monogermanic acid.

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867. *Submicro-methods for the Analysis of Organic Compounds. Part I. The Determination of Nitrogen.*

By R. BELCHER, T. S. WEST, and M. WILLIAMS.

Nitrogen in organic compounds is determined by decomposing a sample, about 50 μg., in a sealed tube and titrating the ammonia thus formed with a standard solution of sodium hypochlorite.

The results are comparable in accuracy with those obtained on the micro-scale.

SEVERAL years ago we began investigations to devise a system of organic analysis for the determination of elements and functional groups requiring sample weights of about 0·05 mg. (50 μg.). This weight was chosen because it was considered to be the smallest that could be practically manipulated without use of magnifying lenses: *e.g.*, 0·05 mg. of a sucrose crystal is only just visible to the naked eye.

Several methods have now been perfected: those developed so far are based on classical principles and the only specialised apparatus required is the balance previously described [1] and a micrometer-syringe burette.

[1] Asbury, Belcher, and West, *Mikrochim. Acta*, 1956, 598.

Submicro-methods should have far-reaching applications, particularly in biochemistry, physiological chemistry, or wherever only minute amounts of material are available. They should also prove invaluable for use in conjunction with modern techniques such as vapour-phase chromatography where minute samples of high purity can be obtained. They are not intended to replace the conventional micro-methods preferable when sufficient material is available.

Determination of Nitrogen.—After consideration of modifications of Kjeldahl's method it was concluded that the best means of decomposition would be by digestion in a sealed tube.[2] This has several advantages over more conventional methods of decomposition; complete decomposition is more certain, catalysts and other additions (potassium sulphate) are unnecessary, the temperature can be controlled, and, most important in view of the scale, risk of atmospheric contamination is eliminated. For completing the determination, titration of the ammonia with standard hypochlorite was chosen.[3] This titrant had previously been used on the micro-scale [4] and offered the advantage that the digestion and the titration could be done in the same vessel.

Since this work was started Kirk and his co-workers have reported the successful determination of μg. amounts of nitrogen [5] and phosphorus.[6] Much of their analysis was on biological material, with relatively large samples. Kirk *et al.* checked the method for nitrogen by analysing some pure organic compounds. Satisfactory results were obtained on sample weights similar to those described below; sealed-tube digestion was also used for decomposition, but a diffusion method followed by an acid–base titration was used for determination of the ammonia.

Our general procedure was developed stepwise, starting from simple ammonium salts in pure solution, to eliminate errors associated with a particular stage. The most serious difficulty was to find a simple method for adjusting the pH of the digest (the hypochlorite titration is only satisfactory from pH 7·5 to 9·6). Organic indicators reacted with hypochlorite and yielded variable blanks, but satisfactory adjustment was obtained by the addition of a mercuric salt; [4] the precipitation of mercuric oxide indicated the approach of the neutralisation point and final adjustment was obtained by the use of a sodium hydrogen carbonate buffer. When the pH was too low a yellow colour developed owing to decomposition of hypochlorite; at too high a pH, the mercuric oxide precipitate did not dissolve when potassium bromide was added.

An electrically heated metal block drilled to accommodate the digestion tubes was used for decomposition. Satisfactory recoveries were obtained over the range 400—450°. A period of 30 min. was adequate; but a longer time (60 min.) showed no significant differences. Below temperatures of about 380°, decomposition was incomplete, and above 500° there were losses of ammonia. The temperature range 420—430° was always used subsequently. These findings agree substantially with those of Kirk *et al.*[5]

A series of compounds was analysed by this procedure; the results are included in the Table, Column A, and in most cases are the average of 10 determinations. Although the absolute errors were generally within 0·3%, nearly all were negative. These results were calculated on the basis of the hypochlorite solution standardised against thiosulphate which had been standardised in turn against potassium iodate. When the hypochlorite solution was standardised directly against a pure ammonium salt, the normality was always slightly higher. The results in Column B have been calculated from hypochlorite standardised in this way. This empirical standardisation of hypochlorite has been advocated by earlier investigators [7, 8] and in view of our own results is recommended.

[2] White and Long, *Analyt. Chem.*, 1951, **23**, 363.
[3] Kolthoff and Stenger, *ibid.*, 1935, **7**, 79.
[4] Belcher and Bhatty, *Mikrochim. Acta*, 1956, 1183.
[5] Grunbaum, Schaffer, and Kirk, *Analyt. Chem.*, 1952, **24**, 1487.
[6] Schaffer, Long, and Kirk, *ibid.*, 1953, **25**, 343.
[7] Wolfel, *Z. analyt. Chem.*, 1932, **90**, 170.
[8] Willard and Cake, *J. Amer. Chem. Soc.*, 1920, **42**, 2646.

Compound	N, calc. (%)	A		B	
		N, found (%)	Δ *	N, found (%)	Δ *
Acetanilide	10·36	10·16	0·20	10·37	0·20
Phenacetin	7·82	7·69	0·16	7·85	0·15
Hippuric acid	7·82	7·78	0·21	7·93	0·16
4-Benzylideneaminodiphenyl	5·45	5·40	0·25	5·51	0·24
Diphenylacetonitrile	7·25	7·08	0·12	7·23	0·15
s-Diphenylurea	13·21	13·04	0·20	13·30	0·20
α-Benzoin oxime	6·16	6·05	0·20	6·17	0·20
s-Diphenylguanidine	19·89	19·79	0·20	20·18	0·19
Benzamide	11·57	11·41	0·19	11·64	0·19
o-Tolidine	13·20	12·86	0·20	13·12	0·20

Column A. Hypochlorite standardised against standard thiosulphate.
Column B. Hypochlorite standardised against ammonium sulphate.
* Standard deviation.

Experimental

A. *Reagents.—Sulphuric acid.* Microanalytical reagent (M.A.R.).

Mercuric sulphate. 2% Solution, prepared by adding a few drops of M.A.R. sulphuric acid to 2 g. of M.A.R. mercuric sulphate, followed by about 20 ml. of distilled water. The mixture was thoroughly stirred, and more distilled water added, with continued stirring, to dissolve the last traces of solid. The solution was then diluted to 100 ml.

Sodium hydroxide. 2N-Solution prepared by dilution of the standard commercial solution from ampoules.

Sodium hydrogen carbonate. 5% Solution, prepared from " AnalaR " solid.

Potassium bromide. 30% Solution, prepared from " AnalaR " solid.

Sodium hypochlorite. 0·04N-Solution, prepared by diluting the appropriate volume of 10—14% (available chlorine) solution with distilled water. B.D.H. bromine-free reagent was used.

Potassium iodide. 30% Solution, prepared from " AnalaR " solid. The solution was made freshly each day in order to limit the blank caused by decomposition.

Sulphuric acid. 4N-Solution, prepared by dilution of M.A.R. acid.

Sodium thiosulphate. 0·04N-Solution, prepared from " AnalaR " salt.

Indicator. " Thyodene," which could be added as solid and was therefore more convenient than a starch solution.

Ammonium sulphate. " AnalaR " salt was very finely ground with a micro-pestle and mortar and then dried (P_2O_5) under vacuum.

B. *Apparatus.—Ultramicrobalance.* The balance and its operation were as described by Asbury, Belcher, and West.[1]

Digestion tubes. These were of borosilicate glass tubing (13 mm. external diam., 11 mm. internal diam., and 7 cm. length) with a hemispherical seal at one end. They were cleaned by soaking either overnight in chromic acid or for a few minutes in a 5% mixture of hydrofluoric acid (about 40% solution) with Teepol, followed by thorough washing with tap- and then distilled-water. The clean tubes were dried at 120°, and stored over phosphoric oxide. It was important for the glass to be perfectly dry and free from grease, etc., so that none of the small crystals of an ultramicro-sample would stick to the sides of a tube during transfer.

Heating block. This consisted of an electrically heated Dural block drilled with 8 holes to accommodate the digestion tubes.

Centrifuge. An electric semimicro-centrifuge capable of 4000 r.p.m.

Titration equipment. " Agla " micrometer syringes (Burroughs Wellcome & Co.) were employed throughout. Each had a graduated total capacity of 0·5 ml., the individual graduations corresponding to a volume of 0·0002 ml. (*i.e.*, 0·2 μl.). It was possible to estimate to 0·1 μl. without difficulty. In place of the metal needle normally provided, a glass capillary bent at a right angle was sealed on the nozzle of the syringe. It could be used in this form as either a pipette or a burette. A coiled metal spring was always kept over the syringe plunger in practice to prevent the plunger's slipping into the barrel of the syringe without pressure being exerted on it from the micrometer screw-gauge.

Rotating magnetic stirring was employed. Each stirrer consisted of a short thin steel rod sealed into a glass capillary (1 cm. long), a very thin glass capillary (0·5 cm.) being sealed at right angles to the centre of the latter to give a T-shape.

The opened digestion tube, containing the centrifuged digest, was clamped on the surface of

a white tile resting on top of the case containing the electrically operated rotating magnet. A stirrer was added, and the syringe burette was clamped horizontally so that its capillary tip dipped below the surface of the liquid.

To provide standard illumination, a Daylight Blue Bulb (230 v, 60 w, Mazda B.T.H. Single Coil) was enclosed in a dark shade and clamped about one foot above the titration tube at a slight angle to the vertical. This produced an intense white light and enabled the progress of a titration to be watched from above the open end of the tube. The disappearance of the blue starch–iodine colour could be seen readily against the illuminated white tile background.

C. *Recommended Procedures.—Sealed-tube determination of organic nitrogen.* (i) Weighing. The contents of a weighing boat were transferred to an empty digestion tube by holding the boat in tweezers over the mouth of the tube, inverting, and tapping the tweezers supporting the boat on the edges of the tube mouth. The boat was then reinverted, and restored to the scale-pan of the ultramicro-balance. The sides of the digestion tube were well tapped to ensure that all the sample crystals fell to the bottom. During transfer, the tube had to be clamped upright.

For a series of determinations, 8 clean dry digestion tubes (4 for nitrogen and 4 for blank determinations) were placed in a metal-block holder in a desiccator containing phosphoric oxide. The total time to complete these 8 determinations was usually slightly more than 8 hr.

(ii) Digestion. Concentrated sulphuric acid (10 μl.) was added to each digestion tube from a syringe burette, the drop being removed from its tip by touching the latter lightly against the sides near the bottom of the tube. The closed end of the tube was then inserted about 2 cm. into a tight holder consisting of a B19 Quickfit socket lined with asbestos paper, and an oxygen–gas flame applied at a point some 2 cm. from the open end. When the glass was quite molten, the open end was pulled out with clean tweezers and a seal made as near to the main tube as possible.

The sealed tube was placed in a cavity of the block with tweezers and left for 30 min. at 420—430°. After digestion, the sealed tubes were removed from the heating block with tweezers and allowed to cool for a few minutes. They were then centrifuged thoroughly (about 5 min.) and returned to the holder in the phosphoric oxide desiccator.

Although the glass was thin where the tube was sealed, the pressure developed during digestion was normally never sufficient to cause an explosion. When a cooled digestion tube was opened, there appeared to be very little, if any, excess of pressure.

(iii) Titration. A scratch was made with a sharp glass knife some 1·5 cm. from the point of sealing and the tube opened by applying a piece of molten soft-glass rod lightly to the moistened scratch. The two portions of the tube were then placed in an oven at 90° for 5 min. to remove any sulphur dioxide from solution in the digest (this would interfere in the titration). After being removed from the oven, the two portions of the digestion tube were allowed to cool for about 1 min. in a metal-block holder in an otherwise empty desiccator.

Distilled water (1 ml.) was taken into a 2 ml. hypodermic syringe (Everett Syringes, metal nozzle) and 0·5 ml. washed down the sides of the main portion of the opened digestion tube. The tip of the digestion tube was washed out with two 0·25 ml. portions of distilled water from the hypodermic syringe, these being swilled over the inside surface of the tip several times before transfer to the main tube by means of a capillary dropper containing a 1 ml. reservoir bulb. The final contents of the main tube were gently swilled over its inside by tilting and rotating it carefully a few times.

A T-piece stirrer and 2% mercuric sulphate solution (1 drop) were added to the main tube (now a titration tube), the light was switched on, and the stirrer started. 2N-Sodium hydroxide was run in fairly quickly from a syringe burette until the first sign of a white turbidity, and then more slowly until the capillary tip of the syringe burette and stirrer were obscured from view by a yellowish-white cloudy precipitate. The alkali was then added very slowly. When crystalline material became visible against the cloudy background of colloidal material, further additions of sodium hydroxide were made only a little at a time. As soon as the background cloudiness cleared, no more alkali was added. It was important to avoid the addition of excess of alkali at this stage. 5% Sodium hydrogen carbonate (1 drop) and 30% potassium iodide (2 drops) were added at once, so that the solid material could not adsorb much alkali and be rendered insoluble. If some solid remained undissolved after being stirred for a few minutes, further additions of bromide and bicarbonate were made.

When a clear titration medium had been obtained, a known amount (about 150% of theoretical) of standard 0·04N-sodium hypochlorite solution was run in from a syringe burette

with stirring throughout. The titration tube was then placed in a metal-block holder in the empty desiccator for 5 min. while oxidation of the ammonia was completed. After being removed from the desiccator and again clamped above the stirrer motor, the latter was switched on, freshly prepared 30% potassium iodide (1 drop) added, the solution acidified with 4N-sulphuric acid (1 drop), and the liberated iodine titrated at a *slow* steady rate with standard 0·04N-sodium thiosulphate solution until the yellow colour had nearly disappeared. A little solid Thyodene was added from the end of a micro-spatula, the light was switched on, and the titration completed with further 0·04N-thiosulphate solution. The disappearance of the blue starch–iodine colour was best seen from above the open end of the titration tube against the illuminated white tile. It was essential not to titrate very quickly.

The blank determination was carried out as described above, except that as there was no nitrogenous organic compound present no crystalline material was formed. After the appearance of the dense yellowish-white cloudy precipitate, alkali was added very slowly until the first sign of clearance was noted. Further addition of sodium hydroxide was made a little at a time. In the pauses between these additions, time was allowed for the alkali to mix into the whole system; the addition of alkali was stopped when the cloudiness disappeared. The nitrogen and blank titrations were done alternately, the sodium hydroxide, sodium hypochlorite, and sodium thiosulphate syringe burettes being refilled after each blank titration. Blanks varying between 2 and 5 μl. of 0·04N-hypochlorite have been found; they should not exceed 6 μl. The time between the opening of a sealed tube and reaching the iodometric end-point was about 30 min. Hence, the contents of the syringe burettes were only exposed to the laboratory conditions of light, etc., for about 1 hr. before being replaced.

1 μl. of 0·04N-NaOBr (*i.e.*, NaOCl) = 0·1868 μg. of nitrogen. Hence,

$$\text{nitrogen in sample} = (V - V') \times f \times 18{\cdot}68/W\%$$

where W = weight of sample taken (in μg.), f = normality factor of the 0·04N-sodium hypochlorite solution, V and V' = unconsumed 0·04N-hypochlorite in the blank and in the nitrogen determination, respectively (μl.).

Standardisation of Sodium Hypochlorite.—A weighed sample (about 50 μg.) of ammonium sulphate was transferred to a titration-type tube and digestion acid (10 μl.) run in from a syringe burette, the drop being taken from the burette tip by touching it lightly against the sides of a titration tube. Distilled water (1 ml.) was then added from a graduated hypodermic syringe, a T-piece stirrer introduced, and the acid neutralised as before. The oxidimetric titration of the ammonia was also done as outlined above.

The blank titrations were carried out in exactly the same way, except that no ammonium sulphate was present.

The nitrogen content of ammonium sulphate being taken as 21·19%, then:

Normality of NaOCl (*i.e.*, NaOBr) = $21{\cdot}19W \times 0{\cdot}04/[f(V - V') \times 18{\cdot}68]$N where W = weight of ammonium sulphate taken (in μg.), V and V' are analogous to V and V' in the hypochlorite titrations (above), and f = ratio of concentration of hypochlorite to that of thiosulphate (see below).

A series of 5 standardisations, with 5 blanks, was usually carried out in this way and the average value taken for the normality of the sodium hypochlorite solution. The normality of the sodium thiosulphate solution was then calculated from the known ratio of the concentrations of the two titrants (*i.e.*, f). The standard deviation of a series of standardisations was 0·009. In one typical series the average blank was 2·8 μl., the largest deviation from this mean value being 0·4 μl. (*i.e.*, 0·07 μg. of nitrogen).

Determination of the Ratio of the Concentrations of the Hypochlorite and Thiosulphate Solutions.—0·04N-Sodium hypochlorite (40 μl.) was run into a titration-type tube containing distilled water (1 ml.) and a T-piece stirrer inserted. The stirrer motor was switched on, freshly prepared 30% potassium iodide (1 drop) added, the solution acidified with 4N-sulphuric acid (1 drop), and the liberated iodine titrated with 0·04N-sodium thiosulphate, Thyodene being used as indicator in the manner described above.

Hence:

$$f = \frac{\text{Concn. of NaOCl solution}}{\text{Concn. of } Na_2S_2O_3 \text{ solution}} = \frac{40}{V}$$

where V = volume (μl.) of 0·04N-thiosulphate required to titrate the liberated iodine.

A series of 5 titrations was always carried out, and the average sodium thiosulphate titre taken for *V*.

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CHEMISTRY DEPARTMENT, THE UNIVERSITY, BIRMINGHAM, 15. [*Received, April 3rd*, 1957.]

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868. *The Hydrolysis of Sodium Trithiocarbonate and its Reaction with Ethanol.*

By G. INGRAM and B. A. TOMS.

The hydrolysis of the CS_3^{2-} ion has been elucidated by investigating reactions of sodium trithiocarbonate with HO^-, H^+, Ag^+, Tl^+, and Pb^{2+} ions and with aniline, using chemical, potentiometric, and spectroscopic methods. The analogous process of ethanolysis, which has not previously been described and in which sodium ethyl xanthate is produced, has also been studied. Some properties of silver, lead, and thallous trithiocarbonates are recorded, and the existence of sodium trithiopercarbonate is inferred. Possible mechanisms for basic reactions are discussed, and a comprehensive scheme is presented which shows the relation between sodium trithiocarbonate and sodium ethyl xanthate and also correlates the formation, hydrolysis, and decomposition by hydroxyl ions, of both these compounds.

TRITHIOCARBONIC ACID, H_2CS_3, and some of its salts were first recognized early in the last century, but knowledge of such compounds is still fragmentary.[1] Much of the published literature deals chiefly with the preparation and identification of individual compounds, and systematic investigation of their properties has been hindered by the practical difficulty of isolating and preserving pure specimens, for the trithiocarbonates are prone to decomposition, especially in air. We have obtained ample pure sodium trithiocarbonate by a new method based on classical reactions.

Some properties of silver, lead, and thallous trithiocarbonates are discussed here incidentally, but we shall be concerned mainly with reactions of sodium trithiocarbonate in aqueous and ethanolic solutions and particularly with the hydrolysis and ethanolysis of the CS_3^{2-} ion. Our interest in these topics arises from the production of sodium trithiocarbonate in the cellulosic solution from which viscose rayon is manufactured,[2] by a side-reaction between carbon disulphide and sodium hydroxide.

The complex hydrolysis of alkali-metal trithiocarbonates has been studied by Berzelius,[3] Tarugi and Magri,[4] Yeoman,[5] and others, but its mechanism remains obscure, though it is generally thought to depend, like thermal decomposition, on the initial step: $CS_3^{2-} \longrightarrow CS_2 + S^{2-}$. The present investigation has led to a different and more comprehensive interpretation. We have also discovered production of sodium ethyl xanthate from the CS_3^{2-} ion and ethanol and believe we may have detected the trithiopercarbonate ion, COS_3^{2-}.

EXPERIMENTAL

Materials.—Metal salts, alkali hydroxides, mineral acids, carbon disulphide, aniline, and hydrogen peroxide (" 100-volume ") were of " AnalaR " quality. Sodium hydrogen sulphide was prepared by Rule's method.[6] Ethanol (" absolute " alcohol B.P.), acetone (not less than 95% distilled between 55·5° and 56·5°; d_4^{20} 0·790—0·794), and anhydrous ether (b. range 34·0—35·0°; d_4^{20} 0·713—0·714°) were used, generally without further purification. Hydrogen sulphide

[1] See, *e.g.*, Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., London, 1947, Vol. VI, p. 119.
[2] Cross, Bevan, and Beadle, *Ber.*, 1893, **26**, 1090, 2524; 1901, **34**, 1513.
[3] Berzelius, *Ann. Chim. Phys.*, 1820, **6**, 450.
[4] Tarugi and Magri, *Gazzetta*, 1909, **39**, I, 405.
[5] Yeoman, *J.*, 1921, **119**, 38.
[6] Rule, *J.*, 1911, **99**, 558.

was generated from ferrous sulphide, washed with sodium sulphide solution, and dried (fused $CaCl_2$); carbon oxysulphide was obtained by the action of 50% sulphuric acid on saturated aqueous potassium thiocyanate.[7] Distilled water was used throughout.

Gas Analysis.—Gaseous products were swept from a reaction mixture by a slow stream of nitrogen which then passed through bubblers containing selectively absorbent liquids. Each absorbent (100 ml.) was distributed between 2 or 3 adjacent bubblers, and groups of bubblers were segregated by suitable traps. (*a*) Hydrogen sulphide, (*b*) carbon dioxide, and (*c*) carbon disulphide vapour were extracted from the carrier gas in that order, (*a*) by solution of lead acetate (10 g.) in glacial acetic acid (20 g.) and water (80 ml.) (lead sulphide was weighed), (*b*) by standard sodium hydroxide solution (titration [8]), and (*c*) by potassium hydroxide (10 g.) in 90—95% ethanol (100 ml.) (potassium ethyl xanthate determined iodometrically [9]).

Potentiometry.—Aqueous (and, where possible, ethanolic) solutions of sodium salts (carbonate, hydrogen carbonate, ethyl carbonate, hydroxide, hydrogen sulphide, sulphide, disulphide trithiocarbonate, perthiocarbonate, ethyl xanthate) were titrated potentiometrically against standard aqueous solutions of hydrochloric acid, silver nitrate, and thallous sulphate (and nitrate). The cell systems used are shown in the Table.

Titrant	Indicator electrode	Reference electrode
H^+	Sb or glass	Saturated calomel
Ag^+	Ag	Saturated $HgCl_2$ or Ag–sat. aq. AgCl containing $AgNO_3$ and HNO_3.[10]
Tl^+	Sb or Tl	Sat. $HgCl_2$

Titrations were carried out at room temperature, a valve electrometer (Cambridge pH Meter) being used. The solution was stirred continuously, and the free surface (of aqueous solutions) was covered with a layer of toluene.

Equivalent weights were deduced from titrations with standard hydrochloric acid.

Absorption Spectroscopy.—Optical densities in the 200—600 mμ wavelength region were measured, at room temperature, by means of a photoelectric quartz spectrophotometer (Unicam Model SP. 500). The solutions were contained in quartz cells (width, 1 cm.; thickness, 0·2 or 1 cm.) fitted with lids.

Elementary Analysis.—The sulphur contents of metal trithiocarbonates could not be determined accurately by a rapid micro-combustion method [11] because the carbon disulphide released ($MCS_3 \longrightarrow MS + CS_2$) was not completely oxidized in the (empty) combustion tube. However, in the corresponding method for estimating carbon and hydrogen,[12] the carbon disulphide was completely oxidized on reaction with the hot silver packing of the combustion tube.

The sulphur content of sodium trithiocarbonate was estimated by dissolving the sample (0·5 g.) in 25N-sodium hydroxide (100 ml.) and adding an excess of hydrogen peroxide (20 ml.). The solution was then heated to promote decomposition ($CS_3^{2-} + 6HO^- \longrightarrow 3S^{2-} + CO_3^{2-} + 3H_2O$), and the sulphate produced was weighed as the barium salt.

Sodium was determined by igniting a specimen with 50% sulphuric acid and weighing the residual sodium sulphate.

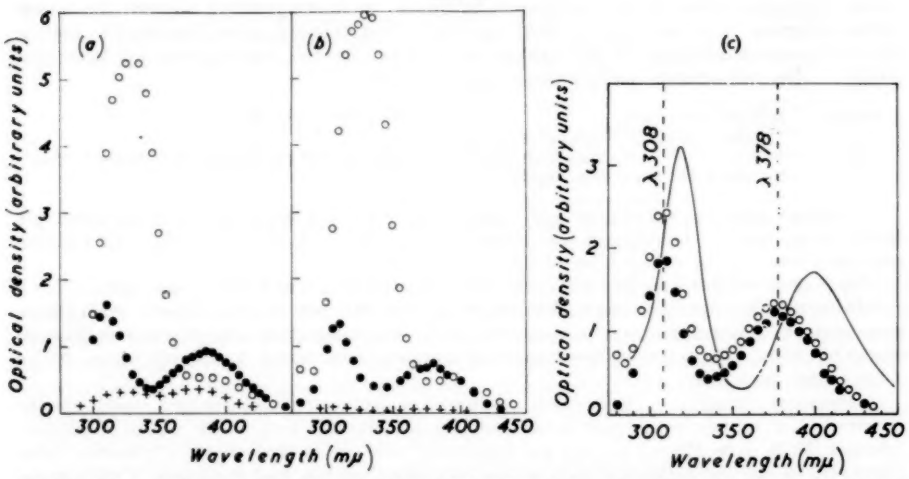
Preparation of Sodium Trithiocarbonate.—(a) *From sodium sulphide.* Sodium sulphide ($9H_2O$; 30 g.), water (60 ml.), and carbon disulphide (10 ml.) were shaken in a glass-stoppered flask (100 ml. capacity; air-space small) at room temperature for 36—48 hr. The resulting red solution (*ca.* 85 ml.) and residual carbon disulphide (2—3 ml.) were poured into acetone (750 ml.) and the whole was shaken. The red, oily, lower layer (*ca.* 30 ml.) was run into acetone (250 ml.). The upper layer was discarded; it exhibited striking changes of colour (yellow $\longrightarrow$ dark green $\longrightarrow$ colourless) as dissolved sodium hydrogen sulphide was oxidized: $2HS^- \longrightarrow S_2^{2-} \longrightarrow S_2O_3^{2-}$ (S_2^{2-} gives a green colour with acetone). The red oil and acetone were stirred together for a few minutes and then the acetone was decanted.

The red oil (now *ca.* 25 ml.) was extracted, at room temperature, with ethanol (4 × 250 ml.). Each extraction took about 3 min. and was effected by vigorous stirring; as extraction proceeded,

[7] Klason, *J. prakt. Chem.*, 1887, **36**, 66.
[8] Martin and Green, *Ind. Eng. Chem. Analyt.*, 1933, **5**, 114.
[9] Jacobs, "Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," Interscience Publ. Inc., New York, 1944, p. 265.
[10] Ingram, *Mikrochim. Acta*, 1956, 877.
[11] Belcher and Ingram, *Analyt. Chim. Acta*, 1952, **7**, 319.
[12] *Idem, ibid.*, 1950, **4**, 118.

the oil solidified. The combined extracts were filtered through sintered glass (porosity 3), and residual solid was discarded. The entire orange filtrate was then stirred vigorously while ether (1 l.) was added as quickly as possible. Crystallization, which began after a few seconds, was allowed to continue, with intermittent stirring, for about 15 min. The yellow rectangular plates were filtered off, drained free from mother-liquor (which contained sodium ethyl xanthate), and washed with ether. When the ether had been removed, the crystals were stored *in vacuo*, or in dry nitrogen, or under liquid carbon disulphide in a well-stoppered bottle. (These operations were carried out as rapidly as possible so as to minimize exposure of the crystals to the atmosphere from which they very quickly absorbed moisture and carbon dioxide. Rapid working also reduced the loss of sodium trithiocarbonate caused by its reaction with ethanol.)

FIG. 1.



(*a*) *Absorption spectrum of a solution of sodium trithiocarbonate in water when freshly prepared* (○) *and after* 3·5 (●) *and* 21 *hours* (+) *at room temperature.*
(*b*) *Absorption spectrum of a solution of sodium trithiocarbonate in* 2N*-sodium hydroxide when freshly prepared* (○) *and after* 15 (●) *and* 25 *days* (+) *at* 25°.
(*c*) *Absorption spectra of an old solution of sodium trithiocarbonate in* 2N*-sodium hydroxide* (●) *and of a solution of sodium sulphide which had been treated with carbon oxysulphide and then oxidized* (○). *The curve represents the absorption spectrum of a solution of sodium tetrathiopercarbonate.*

The crystals consisted of *sodium trithiocarbonate dihydrate* (A) (10—15 g., 40—60%) (Found: C, 6·3, 6·3; H, 2·0, 2·1; S, —, 48·8; Na, 23·9, 23·9%; equiv., 95·0. $Na_2CS_3,2H_2O$ requires C, 6·3; H, 2·1; S, 50·5; Na, 24·2%; equiv., 95·1).

Apricot-coloured needles of trihydrate and salmon-pink needles of tetrahydrate were obtained by using less acetone in the initial treatment of the reaction mixture or by adding water to the filtered ethanolic solution, but the conditions for producing these higher hydrates appeared to be critical. Attempts to prepare a monohydrate were unsuccessful, but anhydrous sodium trithiocarbonate (B) was obtained as a pink powder by drying the di-, tri-, or tetrahydrate for 24—48 hr. in a vacuum at 40—50° (Found: S, 59·4; Na, 29·8%; equiv., 77·1. Calc. for Na_2CS_3: S, 62·4; Na, 29·9%; equiv., 77·0).

(b) *From sodium hydroxide.* Sodium hydroxide (16 g.), water (80 ml.), and carbon disulphide (12 ml.) were shaken in a glass-stoppered 100-ml. flask at room temperature for 72—120 hr. Treatment as described in (a) gave yellow needles (10—15 g., 40—60%) of $Na_2CS_3,2H_2O$ or $Na_2H_2COS_3,H_2O$ (Found: C, 6·1, 6·6; H, 3·1, 2·2; S, —, 50·2; Na, 23·8, 24·1%; equiv., 95·0). Recrystallization from ethanol–ether gave rectangular plates which were indistinguishable from those of (A), but this change of habit could not be reversed.

Reactions of Sodium Trithiocarbonate in Aqueous Solution.—(a) *With water.* (i) A solution of the dihydrate (A) (0·21 g.; $1·1 \times 10^{-3}$ mole) in boiled distilled water (50 ml.) was kept under

nitrogen for 72 hr. at room temperature. Hydrolysis produced $<0{\cdot}1 \times 10^{-3}$ mole of each of hydrogen sulphide, carbon disulphide, and sodium carbonate (or hydrogen carbonate).

(ii) A solution of dihydrate (A) (0·19 g.; $1{\cdot}0 \times 10^{-3}$ mole) in boiled distilled water (50 ml.) was heated in a stoppered flask (*ca.* 50 ml. capacity; air-space small) on a water-bath at about 90° (internal), its colour changing from orange to green. After 2·5 hr. the solution was cooled and treated with 5N-hydrochloric acid (15 ml.): hydrogen sulphide ($1{\cdot}7 \times 10^{-3}$ moles) and carbon dioxide ($0{\cdot}47 \times 10^{-3}$ mole) were released.

(iii) The absorption spectrum of sodium trithiocarbonate in aqueous solution was observed at wavelengths between 250 and 450 mμ for solutions containing about 5×10^{-4} mole/l., and at wavelengths between 400 and 600 mμ for those containing about 5×10^{-2} mole/l. In agreement with previous work,[13], three absorption bands were found. Two of these, with peaks at 325—330 and at 500 mμ, respectively, were well defined; in a freshly-made solution, the third band appeared as a " shoulder " extending from 375 to 400 mμ, approximately. The absorption at wavelengths greater than 300 mμ gradually disappeared (Fig. 1*a*). The absorption band with its peak at 325—330 mμ disappeared rapidly and was replaced, after 3—4 hr., by a well-defined band with its peak at 308—310 mμ, whilst absorption in the 375—400 mμ region increased until a well-defined band with its peak at about 385 mμ had been formed. Later, both of the " new " absorption bands disappeared.

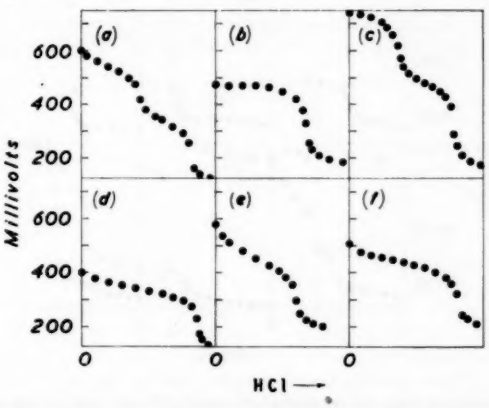


FIG. 2. *Potentiometric titration curves obtained by adding 0·1N-hydrochloric acid to aqueous solutions containing* (*a*) Na_2CO_3, (*b*) Na_2CS_3, (*c*) Na_2S, (*d*) $NaHCO_3$, (*e*) $NaHCO_3$ *and* NaSH *in equimolar proportion*, (*f*) NaSH.

For comparison, samples of sodium tetrathiopercarbonate were prepared by reaction between carbon disulphide and sodium disulphide and by adding sulphur to a solution of sodium trithiocarbonate, as described by Yeoman.[5] The absorption spectrum of this compound (0·01 g.) in water (100 ml.) contained well-defined bands [13] with peaks at 320 and 400 mμ (see Fig. 1*c*).

(b) *With hydrogen ions.* (i) The dihydrate (A) (0·11 g.; $0{\cdot}58 \times 10^{-3}$ mole) in water (75 ml.) was decomposed, at room temperature, by adding 0·1N-hydrochloric acid (30 ml.): hydrogen sulphide ($0{\cdot}56 \times 10^{-3}$ mole) and carbon disulphide ($0{\cdot}56 \times 10^{-3}$ mole) were released, but not carbon oxysulphide.

When this reaction was observed potentiometrically at room temperature and at 0°, both the antimony and the glass electrode gave one-step titration curves, the former showing the equivalence point at about 300 mv, and the latter at about 165 mv. These titration curves, and particularly the curve obtained with the antimony electrode at room temperature (Fig. 2*b*), were compared with curves obtained by titrating various model aqueous solutions under the same conditions. There was a striking resemblance between the trithiocarbonate curve and those given by sodium hydrogen sulphide solution (Fig. 2*f*) and by a freshly-made solution containing sodium hydrogen sulphide and sodium hydrogen carbonate in equimolar proportion (Fig. 2*e*). In contrast, the curves given by sodium sulphide (Fig. 2*c*) and sodium carbonate (Fig. 2*a*) each had two steps (corresponding to HO^- and HS^- in the case of sulphide, and to HO^- and HCO_3^- in the case of carbonate), while sodium hydrogen carbonate gave a distinctive one-step curve with the equivalence point at about 200 mv (Fig. 2*d*).

[13] Halban, Mackert, and Ott, *Z. Elektrochem.*, 1923, **29**, 445; Atsuki and Takata, *J. Soc. Chem. Ind., Japan*, 1940, **43**, 394B; Schauenstein and Treiber, *Melliand Textilber.*, 1951, **32**, 43.

(ii) When carbon dioxide was bubbled through a solution of dihydrate (A) (0·49 g.; $2·6 \times 10^{-3}$ mole) in water (50 ml.) for 1 hr. at room temperature, hydrogen sulphide ($2·4 \times 10^{-3}$ mole) and carbon disulphide were released. After nitrogen had been bubbled through it for 30 min., the residual solution contained sodium hydrogen carbonate only ($5·1 \times 10^{-3}$ mole).

(iii) Hydrogen sulphide was bubbled through a solution of dihydrate (A) (0·13 g.; $0·69 \times 10^{-3}$ mole) in water (75 ml.) for about 20 min. The solution became green, carbon disulphide appeared, and it was evident that the trithiocarbonate had been decomposed. The excess of hydrogen sulphide was removed by bubbling nitrogen through the solution for about 60 min., and then the solution was made up to 100 ml. with water. The solution contained sodium hydrogen sulphide, the amount of which ($1·4 \times 10^{-3}$ mole) was determined by bubbling carbon dioxide through a sample (50 ml.) and collecting the hydrogen sulphide released (the amount of sodium hydrogen carbonate in the residual solution was also determined); another sample of the hydrogen sulphide solution was titrated with 0·1N-iodine solution. (Consistent results were obtained by the different methods.)

(c) *With hydroxyl ions.* (i) A solution of dihydrate (A) (0·19 g.; $1·0 \times 10^{-3}$ mole) in aqueous 0·1N-sodium hydroxide (50 ml.) was kept under nitrogen for 72 hr. at room temperature, then

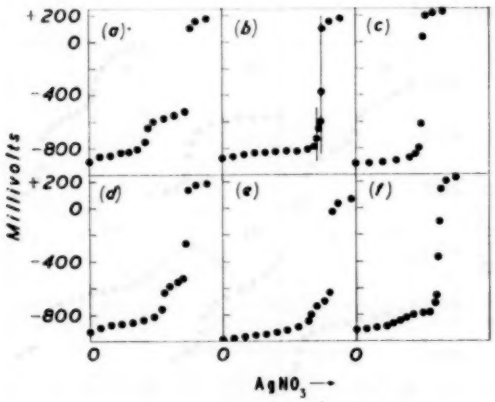


FIG. 3. *Potentiometric titration curves obtained by adding 0·1N-silver nitrate to aqueous solutions containing* (*a*) NaSH, (*b*) Na_2CS_3, (*c*) Na_2S, (*d*) Na_2CS_3 *and* NaSH *in equimolar proportion*, (*e*) NaSH *and* $NaHCO_3$ *in the molar proportion* 2 : 1, (*f*) Na_2CS_3 *and* Na_2S *in equimolar proportion.*

treated with 5N-hydrochloric acid (15 ml.) which released hydrogen sulphide ($0·95 \times 10^{-3}$ mole), carbon disulphide, and carbon dioxide ($0·17 \times 10^{-3}$ mole). Combined sulphur (polysulphides ?) in the residual solution was oxidized and collected as barium sulphate ($0·10 \times 10^{-3}$ mole).

(ii) A solution of dihydrate (A) ($1·0 \times 10^{-3}$ mole) in aqueous 0·1N-sodium hydroxide (50 ml.) was heated, under reflux, for 3 hr. at about 90°, then cooled and treated with 5N-hydrochloric acid (15 ml.): hydrogen sulphide ($2·8 \times 10^{-3}$ mole), carbon disulphide (a trace), and carbon dioxide ($0·94 \times 10^{-3}$ mole) were released. The residual solution contained combined sulphur ($0·15 \times 10^{-3}$ mole).

(iii) When dissolved in aqueous 0·1—3N-sodium hydroxide, sodium trithiocarbonate gave the same absorption spectrum as in aqueous solution (see p. 4331). The spectrum changed with time, but more slowly than in aqueous solution, and the rate of change varied inversely with the concentration of sodium hydroxide. Fig. 1*b* indicates how absorption in the 250—450 mμ region altered when a solution of dihydrate (A) (0·01 g.) in 2N-sodium hydroxide (100 ml.) was kept at 25°: two well-defined bands, with peaks at 308 and 378 mμ, developed after about 2 weeks, persisted for more than a week, but eventually disappeared.

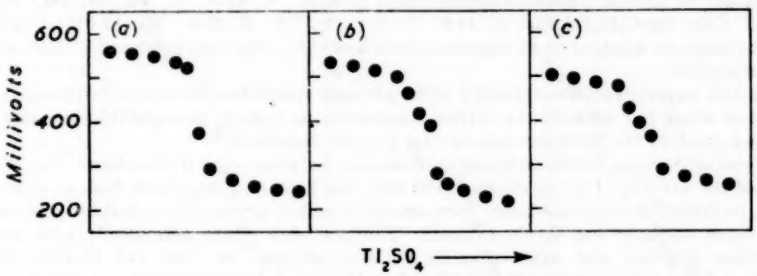
A solution of dihydrate (A) (0·4 g.) in N-sodium hydroxide (100 ml.) was heated on a boiling-water bath; a sample (3 ml.) was withdrawn hourly, diluted with N-sodium hydroxide (97 ml.), and examined spectrophotometrically (250—450 mμ region only). The original absorption bands, with peaks at 325—330 and 375—400 mμ, gradually disappeared and had almost vanished after 7 hours' heating; but the appearance of " new " bands was not observed. However, when the several (diluted) samples were kept at room temperature, two bands with peaks at 308 and 378 mμ developed eventually in every case. It seemed reasonable to conclude that these bands should be assigned to thermolabile ion(s) produced by oxidation.

A solution of sodium tetrathiopercarbonate in 0·1N-sodium hydroxide gave the same absorption spectrum as an aqueous solution of that salt (see p. 4331).

(d) *With silver nitrate.* (i) A trace of silver nitrate gave a dark red colour with a fresh aqueous solution of dihydrate (A). Further addition of silver nitrate produced hydrogen sulphide and a precipitate of silver sulphide (Found: Ag, 86·6. Calc. for Ag_2S: Ag, 87·2%). When an excess of silver nitrate was present, the amount of silver sulphide increased on storage, probably owing to reaction between silver nitrate and carbon disulphide: $4Ag^+ + CS_2 + 2H_2O \longrightarrow 2Ag_2S + 4H^+ + CO_2$.

(ii) When dihydrate (A) (0·092 g.; 0·48 × 10^{-3} mole) in water (100 ml.) was titrated carefully with 0·1N-silver nitrate, a two-step curve, with one equivalence point at about −700 mv and the other at about −250 mv, was obtained (Fig. 3*b*). This curve was compared with curves obtained by titrating various model aqueous solutions under the same conditions. A solution of sodium hydrogen sulphide gave a two-step curve (Fig. 3*a*) with one equivalence point at about −700 mv (corresponding to completion of the reaction: $2HS^- + 2Ag^+ \longrightarrow [2AgSH] \longrightarrow Ag_2S + H_2S$) and the other at about −200 mv (corresponding to completion of the reaction $H_2S + 2Ag^+ \longrightarrow Ag_2S + 2H^+$); a similar curve (Fig. 3*d*) was obtained by titrating a solution containing sodium hydrogen sulphide and sodium trithiocarbonate in equimolar proportion. In contrast, a solution of sodium sulphide gave a one-step curve with the equivalence point at

FIG. 4. *Potentiometric titration curves obtained by adding* 0·1N-*thallous sulphate to aqueous solutions of* (*a*) *freshly crystallized* $Na_2CS_3,2H_2O$, (*b*) *old crystals of* $Na_2CS_3,2H_2O$, (*c*) *pure* $Na_2CS_3,2H_2O$ *and a trace of* NaSH.



about −300 mv (Fig. 3*c*), while a solution containing sodium sulphide and sodium trithiocarbonate in equimolar proportion gave a two-step curve (Fig. 3*f*), with one equivalence point at about −850 mv (corresponding to completion of the reaction: $S^{2-} + 2Ag^+ \longrightarrow Ag_2S$) and the other at about −250 mv (corresponding to completion of the reaction : $CS_3^{2-} + 2Ag^+ \longrightarrow Ag_2S + CS_2$).

A titration curve of very similar form to that given by sodium trithiocarbonate, but with both equivalence-point potentials reduced by about 90 mv, was obtained with a fresh solution containing sodium hydrogen sulphide and sodium hydrogen carbonate in the molar proportion 2 : 1 (Fig. 3*e*); when, however, the molar ratio HS^- : HCO_3^- was 1 : 1 or 1 : 2, the titration curve had only one step owing to elimination of HS^- ions ($HS^- + HCO_3^- \longrightarrow CO_3^{2-} + H_2S$).

(e) *With lead nitrate.* When dilute aqueous solutions of dihydrate (A) and of lead nitrate were mixed, a characteristic crimson-red precipitate of lead trithiocarbonate was produced; [14] this darkened as it decomposed to lead sulphide and carbon disulphide and became black overnight.

(f) *With thallous salts.* (i) Addition of an aqueous solution of thallous sulphate or nitrate to a solution of dihydrate (A) gave a characteristic orange-red precipitate of thallous trithiocarbonate [15] (Found: Tl, 79·0. Calc. for Tl_2CS_3 : Tl, 79·1%). This compound was stable at room temperature, but decomposed to carbon disulphide and thallous sulphide when warmed.

(ii) Solutions of dihydrate (A) (*ca.* 0·1 g.) in water (100 ml.) were titrated potentiometrically (antimony electrode) with 0·1N-thallous sulphate; some of the results were checked by using a thallium electrode, but this was prone to corrosion. Whenever a newly-crystallized specimen of dihydrate was used, the titration curve had one step only, with the equivalence point at

[14] O'Donoghue and Kahan, *J.*, 1906, **89**, 1812.
[15] Picon, *Compt. rend.*, 1932, **195**, 1274.

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about 400 mv (Fig. 4*a*); but if the trithiocarbonate had been kept for 48 hr. or more in a vacuum-desiccator, which was opened and re-evacuated occasionally, the titration curve had one equivalence point at about 450 and another at about 350 mv (Fig. 4*b*): a similar curve was obtained by adding a trace of sodium hydrogen sulphide to a solution of newly-crystallized (A) just before the titration (Fig. 4*c*).

Quantitative experiments showed that the amount of sodium trithiocarbonate in an aqueous solution could not be estimated reliably either by titrating the solution with standard thallous sulphate solution or by adding an excess of that reagent and then collecting and weighing the precipitated thallous trithiocarbonate. It always appeared that some loss of trithiocarbonate had occurred, and this was attributed to decomposition caused by hydrogen ions released from thallous hydrogen sulphide ($2TlSH \longrightarrow Tl_2S + H_2S$; $TlSH + H_2O \longrightarrow TlOH + H_2S$).

(g) *With aniline.* The dihydrate (A) (5 g.; $2{\cdot}6 \times 10^{-2}$ mole), aniline (5 ml.; $5{\cdot}5 \times 10^{-2}$ mole), carbon disulphide (2 drops; about $0{\cdot}15 \times 10^{-2}$ mole), and water (50 ml.) were shaken in a stoppered flask, at room temperature, for 48 hr. The resulting yellow solution and residual aniline were shaken with acetone (500 ml.). The lower layer, a red oil which contained sodium trithiocarbonate (0·3 g.) and sulphide, was discarded; the upper (acetone) layer was evaporated at reduced pressure. The solid residue was extracted with acetone (3×20 ml.): undissolved solid (1·9 g.), which contained sulphide, was filtered off. When the filtrate was evaporated to dryness, a white residue (4·7 g.) remained: this was dissolved in acetone (40 ml.). On addition of ether (500 ml.) to the acetone solution, colourless hygroscopic crystals (2·8 g.) were obtained: these were recrystallized from acetone–ether, dried *in vacuo* (P_2O_5) (final yield, 1 g.), and identified as sodium phenyldithiocarbamate (Found: C, 43·9; H, 3·3; N, 7·0; S, 33·1; Na, 12·1. Calc. for $C_7H_6NS_2Na$: C, 44·0; H, 3·1; N, 7·3; S, 33·5; Na, 12·0%). Addition of thallous sulphate solution to an aqueous solution of this compound produced a characteristic yellow precipitate.

When this experiment was repeated with the same quantities of sodium trithiocarbonate, aniline, and water but without the carbon disulphide, no sodium phenyldithiocarbamate was found, and most of the trithiocarbonate (3·3 g.) was recovered.

Reactions of Sodium Trithiocarbonate in Ethanolic Solution.—(a) *With ethanol.* (i) When a solution of the salt (A) (1 g.) in ethanol (100 ml.) was kept in a stoppered flask at room temperature, its colour changed gradually from orange to yellow-green, a faint turbidity developed, and hydrogen sulphide was slowly evolved. Samples were tested periodically with aqueous 0·1M-thallous sulphate and with ethanolic thallous nitrate. At first, red thallous trithiocarbonate only was thrown down, but after 30—60 min. a brown precipitate, which became red on storage, was obtained. The latter was an intimate mixture of red and black particles, and its colour changed as the black component (thallous hydrogen sulphide and/or sulphide) disappeared. In later tests, the red component was absent, and the precipitate, which appeared black or dark grey, then consisted of a mixture of thallous sulphide and white flocculent thallous ethyl xanthate. After about 5 hr. a portion (5 ml.) of the remaining trithiocarbonate solution was treated with a large excess of ether (150 ml.): sodium hydrogen sulphide and trithiocarbonate (a trace) were precipitated and filtered off. The filtrate was then extracted with water (15 ml.). The presence of sodium ethyl xanthate in the aqueous extract was denoted by the formation of a yellow precipitate with aqueous cupric sulphate.[16]

(ii) A solution of salt (A) (5 g.; $2{\cdot}6 \times 10^{-2}$ mole) in ethanol (250 ml.) was kept in a stoppered flask at room temperature for 120 hr. Carbon dioxide was then bubbled through the solution for 30 min. A bulky precipitate of sodium ethyl carbonate was produced (2·5 g.; $2{\cdot}2 \times 10^{-2}$ mole). From the filtrate most of the ethanol was distilled off at reduced pressure on a water-bath. Addition of ether (75 ml.) to the residual solution (*ca.* 25 ml.) gave a white precipitate, which contained sodium ethyl carbonate; this was filtered off and washed with ether–ethanol (3 : 1 by vol.). The combined filtrate and washings were evaporated on a water-bath at reduced pressure: the residual solid (3·2 g.) consisted almost entirely of sodium ethyl xanthate (*ca.* $2{\cdot}2 \times 10^{-2}$ mole). The crude product was crystallized by dissolving it in ethanol (25 ml.) and adding ether (1000 ml.). The crystals (rectangular plates; 1 g., 30%) were hygroscopic (Found: C, 24·6; H, 4·4; S, 43·9; Na, 15·8. Calc. for $C_3H_5OS_2Na$: C, 25·0; H, 3·5; S, 44·4; Na, 16·0%).

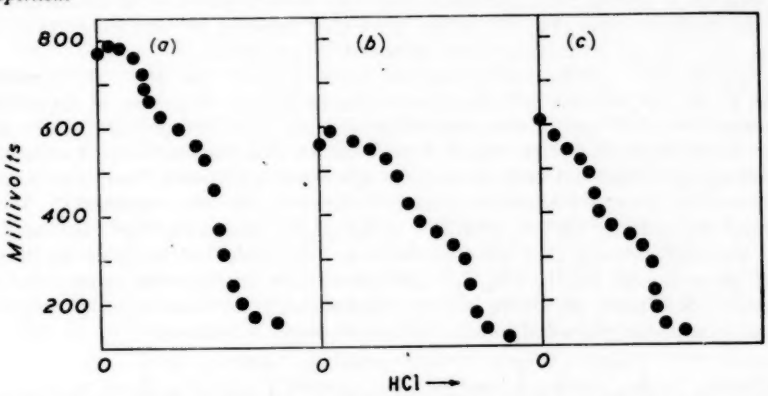
(iii) The anhydrous salt (B) (0·95 g.; $6{\cdot}2 \times 10^{-3}$ mole) was evacuated in a round flask at 10^{-4} mm. Hg, at room temperature, for 3—4 hr., then cooled below −70°, and ethanol (*ca.* 50 ml.), which had previously been redistilled, dried, and degassed, was distilled on to it under

[16] Johnson, *J. Amer. Chem. Soc.*, 1906, **28**, 1211.

vacuum. The flask was sealed and allowed to warm to room temperature. The pink solid became yellow on contact with cold ethanol, but did not dissolve until the temperature had risen considerably. The fresh solution was orange and slightly cloudy; it was kept under vacuum at room temperature for about 24 hr. and then filtered; 0·05 g. of sodium carbonate was collected. On addition of ether (1500 ml.) to the greenish-yellow filtrate, a white precipitate was produced: this was filtered off and proved to be almost pure sodium hydrogen sulphide (0·35 g.; $6·2 \times 10^{-3}$ mole). The ethereal filtrate was then extracted with water (4×25 ml.). Addition of cupric sulphate solution to a portion of the aqueous extract gave a yellow precipitate. A specimen (0·4 g.) of pure sodium ethyl xanthate was isolated by evaporating the aqueous solution to dryness, extracting the residue with acetone, and treating the filtered acetone solution (*ca.* 20 ml.) with ether (1250 ml.).

(iv) Ethanolic solutions of salts (B) (0·06 mole/l.) and (A) (0·05 mole/l.) were kept at 20° in stoppered flasks. From time to time, a sample (25 ml.) of each solution was treated with carbon dioxide for 30 min. (to remove sodium hydrogen sulphide and residual trithiocarbonate), and then titrated with 0·1N-iodine (to determine the amount of sodium ethyl xanthate). This

FIG. 5. *Potentiometric titration curves obtained by adding* 0·1N-*hydrochloric acid (aqueous) to (a) a freshly-prepared solution of sodium trithiocarbonate in ethanol, (b) the same solution when it was 4 hours old, (c) an ethanolic solution containing sodium ethyl xanthate and sodium hydrogen sulphide in equimolar proportion.*



analytical method was not suitable for studying the initial stage of the reaction, but when the conversion of trithiocarbonate exceeded 25% (after about 30 min.) the reactivities of the anhydrous salt and the dihydrate did not differ significantly. The yield of xanthate amounted to 0·75 mol. after 3 hr. and 0·90 mol. after 6 hr.; after 24 hr. it was 1 mol., and the reaction had ended.

(v) Attempts to map the absorption spectrum of sodium trithiocarbonate in ethanol were unsuccessful owing to the rapidity of the reaction between solute and solvent.

(b) *With hydrogen ions.* (i) A solution of dihydrate (A) (1 g.) in ethanol (100 ml.) was kept at room temperature. From time to time, a sample (2·5 ml.) was diluted with ethanol (50 ml.) and titrated potentiometrically (antimony electrode) with aqueous 0·1N-hydrochloric acid. The titration curve had two steps with equivalence points at potentials which depended upon the age of the ethanolic solution. Initially, the equivalence points occurred at approx. 700 and 400 mv (Fig. 5*a*), but after 4 hr. were at about 450 and 250 mv, respectively, and the titration curve (Fig. 5*b*) then resembled that obtained by titrating ethanolic sodium ethyl xanthate and sodium hydrogen sulphide in equimolar proportion under the same conditions (Fig. 5*c*).

(ii) When carbon dioxide was bubbled through a fresh solution of salt (A) (1 g.; $5·3 \times 10^{-3}$ mole) in ethanol (50 ml.), sodium ethyl carbonate was precipitated and after about 30 min. was collected (0·95 g.; $8·5 \times 10^{-3}$ mole) (Found: OEt, 37·0; Na, 20·9%; equiv., 111. Calc. for $C_3H_5O_3Na$: OEt, 40·2; Na, 20·6%; equiv., 112). The filtrate contained small amounts of sodium ethyl xanthate, sodium sulphide (? hydrogen sulphide), and sodium thiosulphate.

In another experiment, carbon dioxide was bubbled through a fresh solution of salt (A)

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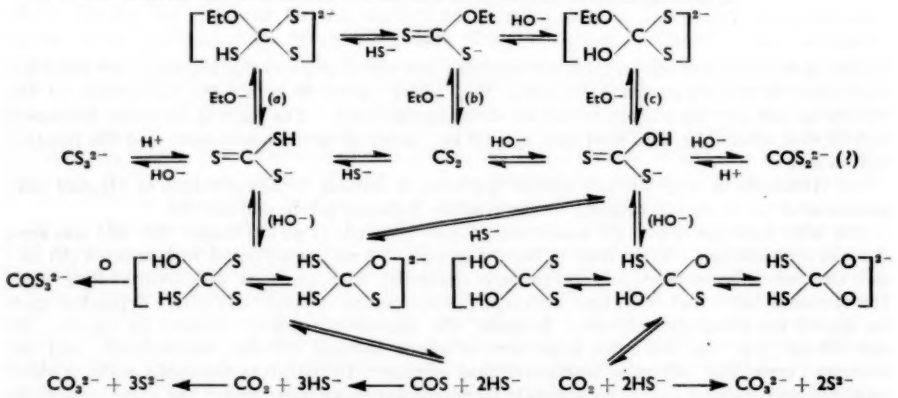
(0·09 g.; 0·47 × 10^{-3} mole) in ethanol (60 ml.) for about 30 min. Hydrogen sulphide (0·47 × 10^{-3} mole) was evolved; the amount of sodium ethyl carbonate (0·93 × 10^{-3} mole) in the residual ethanolic solution was determined by titration with 0·1N-hydrochloric acid.

(iii) Hydrogen sulphide was bubbled through a fresh solution of salt (A) (0·13 g.; 0·69 × 10^{-3} mole) in ethanol (75 ml.) for about 5 min. The solution rapidly became greenish-yellow, and it was evident that the trithiocarbonate had been decomposed. The excess of hydrogen sulphide was removed by bubbling nitrogen through the solution for 90 min., and then the solution was made up to 100 ml. with ethanol. The solution contained sodium hydrogen sulphide (1·3 × 10^{-3} mole, determined by independent methods which gave consistent results). (One sample of the ethanolic solution was treated with carbon dioxide, and the amounts of hydrogen sulphide and sodium ethyl carbonate produced were determined; another sample was titrated with 0·1N-iodine.)

Discussion

Sodium trithiocarbonate in water gives carbon disulphide and sodium sulphide, but our spectrophotometric and potentiometric results show that the hydrolysis is not adequately represented by the simple equilibrium $CS_3^{2-} \rightleftharpoons CS_2 + S^{2-}$. It is not possible, for instance, to account for the observed variation with time of the absorption spectrum of a dilute solution of sodium trithiocarbonate (Fig. 1*a*), or to explain how the reaction between CS_3^{2-} and hydrogen ions (Fig. 2*b*) differs from that between H^+ and CO_3^{2-} (Fig. 2*a*) or S^{2-} (Fig. 2*c*), without postulating some intermediate reactions.

In formulating a satisfactory scheme we have assumed that HS^-, HO^-, and EtO^- can add to the >C=S link and that proton rearrangement can occur in (hypothetical) dihydrogen salts of di- and tri-thio-orthocarbonic acid. The susceptibility of the carbon-sulphur double bond to anionic attack is well known, but the existence of salts of thio-orthocarbonic acids has not been proved, though esters are known,[17] and the occurrence of sodium salts in certain aqueous solutions has previously been surmised.[18] We have introduced reactions of $HCOS_2^-$, HCS_3^-, $(CH_2O_2S_2)^{2-}$, and $(CH_2OS_3)^{2-}$ in the present context primarily because they are convenient and plausible, but we think we may have isolated the ortho-salt $Na_2H_2COS_3,H_2O$ and detected the trithiopercarbonate ion, COS_3^{2-}, in solution. A scheme, which we believe comprehensive for formation, hydrolysis, and reactions in aqueous ethanol of sodium trithiocarbonate, is annexed.



(*a*), (*b*), and (*c*) are alternative routes.

Reactions in Aqueous Solutions.—It has previously been observed,[3,14] and we have confirmed, that when a trithiocarbonate is decomposed by a mineral acid, the products vary with the temperature and composition of the mixture and depend particularly on

[17] Arndt, *Annalen*, 1911, **384**, 322; 1913, **396**, 1.

[18] Herrent and Jnoff, *J. Polymer Sci.*, 1948, **3**, 487; Treiber, Porod, and Lang, *Oesterr. Chem.-Ztg.*, 1952, **53**, 162.

the concentration of hydrogen ions. Thus, if the solid salt is mixed with an excess of concentrated hydrochloric acid at room temperature, trithiocarbonic acid is produced:[19]

$$CS_3^{2-} + H^+ \rightleftharpoons [HCS_3^-] \quad . . . . . (1)$$

$$[HCS_3^-] + H^+ \longrightarrow H_2CS_3 \quad . . . . . (2)$$

but if dilute hydrochloric acid is used, or if the concentrated acid is added slowly to a dilute aqueous solution of sodium trithiocarbonate, carbon disulphide and hydrogen sulphide are obtained:

$$CS_3^{2-} + 2H^+ \longrightarrow CS_2 + H_2S \quad . . . . . (3)$$

This reaction (3) cannot be explained by assuming that (1) and (2) are followed by the decomposition of H_2CS_3 unless chemical and spectroscopic evidence, which proves that sodium trithiocarbonate is extensively hydrolysed in (dilute) solution, is ignored. But before we discuss the mechanism of (3) further it is necessary to review some of our potentiometric results.

When the reaction between CS_3^{2-} and H^+ ions in aqueous solution is followed potentiometrically, a titration curve with *one* step is obtained (Fig. 2*b*), provided the sodium trithiocarbonate is pure. This characteristic curve is easily distinguished from the corresponding curves given by CO_3^{2-} (Fig. 2*a*) and S^{2-} (Fig. 2*c*) both of which have two steps, and also from the one-step curves given by HO^- and by HCO_3^- (Fig. 2*d*), since the equivalence point occurs at significantly different potentials in these cases. There is, however, a remarkable resemblance between the trithiocarbonate titration curve and that given by HS^- (Fig. 2*f*), and both are like the curve given by an equimolar mixture of HS^- and HCO_3^- ions (Fig. 2*e*). Moreover, if fresh solutions containing sodium trithiocarbonate and either sodium hydrogen sulphide or sodium hydrogen carbonate are titrated with acid, the curves obtained (not reproduced here) are almost indistinguishable from each other and from those given separately by CS_3^{2-}, HS^-, or a mixture of HS^- and HCO_3^- ions.

These results show that, under suitable conditions, reaction (3) is closely simulated by the reactions between H^+ and HS^- and between H^+ and ($HS^- + HCO_3^-$), but that it does not involve direct reaction between H^+ and either HO^- or S^{2-}. In seeking a mechanism for (3) which will meet these peculiar requirements, we have been led to conclude that the trithiocarbonate anion must react with water as follows:

$$CS_3^{2-} + H_2O \rightleftharpoons [HCS_3^-] + HO^- \quad . . . . . (4)$$

This reaction, which is analogous to the hydrolysis of the CO_3^{2-} ion, is consistent with equation (1) since it merely involves the transference of a proton from a water molecule to the CS_3^{2-} ion.

However, equation (4) must be an incomplete representation of the hydrolysis of the CS_3^{2-} ion, since it leads only to the prediction of a two-step potentiometric titration curve [like that given by CO_3^{2-} (Fig. 2*a*)] for reaction between sodium trithiocarbonate and dilute hydrochloric acid. This can be remedied by assuming that reaction (4) is followed by

$$[HCS_3^-] + HO^- \rightleftharpoons [HCOS_2^-] + HS^- \quad . . . . . (5)$$

The combination of (4) and (5) leads directly to the simple equilibrium:

$$CS_3^{2-} + H_2O \rightleftharpoons [HCOS_2^-] + HS^- \quad . . . . . (6)$$

and this, as we shall show, is consistent with our potentiometric evidence.

It is not inappropriate to introduce (5) in the present context, for the equilibrium $HCOS_2^- \rightleftharpoons H^+ + COS_2^{2-}$ can be envisaged, and the occurrence of the COS_2^{2-} ion in solutions of sodium trithiocarbonate has been surmised by previous workers.[18] Reaction (5) may be supposed to occur in one (or both) of the following ways:

$$[HCS_3^-] + HO^- \rightleftharpoons HS^- + CS_2 + HO^- \rightleftharpoons [HCOS_2^-] + HS^- \quad . . (5a)$$

$$[HCS_3^-] + HO^- \rightleftharpoons \left[\begin{matrix} HO & & S \\ & C & \\ HS & & S \end{matrix}\right]^{2-} \rightleftharpoons [HCOS_2^-] + HS^- \quad . . . (5b)$$

[19] Mills and Robinson, *J.*, 1928, 2326.

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and these mechanisms emphasize that (6) is complementary to (4) and not merely a convenient alternative reaction. In choosing a reaction to follow (4), we have preferred (5) to $[HCS_3^-] + H_2O \rightleftharpoons [HCOS_2^-] + H_2S$ because it is simpler; and, of course, we have rejected the combination of $[HCS_3^-] \rightleftharpoons CS_2 + HS^-$ and (4) because this would yield equal molar concentrations of HO^- and HS^- ions, which is contrary to the potentiometric evidence.

Having thus decided that the observed reaction (3) depends on the hydrolysis of the CS_3^{2-} ion in accordance with equation (6), we can formulate (3) as follows:

$$CS_3^{2-} + H_2O \rightleftharpoons [HCOS_2^-] + HS^-$$
$$[HCOS_2^-] + H^+ \longrightarrow H_2O + CS_2$$
$$HS^- + H^+ \longrightarrow H_2S$$

This requires hydrogen ions to react only with $HCOS_2^-$ and HS^- ions. And so, since an equimolar mixture of these anions could well be expected to be indistinguishable, potentiometrically, from a similar mixture of HCO_3^- and HS^- ions, or from HS^- ions alone, the above mechanism evidently affords a ready, and complete, explanation of the observed potentiometric characteristics of reaction (3). It also explains how carbon dioxide or hydrogen sulphide decomposes sodium trithiocarbonate in aqueous solution: both these agents yield hydrogen ions ($CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$; $H_2S \rightleftharpoons H^+ + HS^-$), and it can be predicted that the reaction products will be CS_2, H_2S, and $NaHCO_3$ or NaSH in the molar ratios 1 : 1 : 2, as we have found.

The supposition that the hydrolysis of the CS_3^{2-} ion proceeds by the consecutive reactions (4) and (5), and may therefore be represented by equation (6), is also consistent with our observations of the effects of adding Ag^+, Tl^+, or Pb^{2+} ions to (dilute) aqueous solutions of sodium trithiocarbonate. Thallium(I) and lead each yield a characteristic sparingly soluble trithiocarbonate, but with silver only Ag_2S and hydrogen sulphide are obtained. This difference can be explained in terms of (6) and the relative solubilities of the trithiocarbonate and hydrogen sulphide of each metal (the solubility of the metal hydrogen dithiocarbonate does not appear to count, which indicates that, in each case, this salt must be more soluble than either the trithiocarbonate or the hydrogen sulphide).

Evidently, if the solution of sodium trithiocarbonate contains both CS_3^{2-} and HS^- ions, in accordance with equation (6), then the solubility product of thallous or lead hydrogen sulphide must exceed that of the corresponding trithiocarbonate. This inference is confirmed by potentiometric evidence (Figs. 4*b*, 4*c*) which shows that when Tl^+ (or Pb^{2+}) ions are added to a solution of sodium trithiocarbonate in which $[HS^-] > [HCOS_2^-]$ (*e.g.*, because sodium hydrogen sulphide has been added deliberately, or because some decomposition of $HCOS_2^-$ has occurred), precipitation of the heavy-metal trithiocarbonate precedes that of its hydrogen sulphide. And, of course, it follows that if a newly made solution of pure sodium trithiocarbonate is used, then Tl_2CS_3 (or $PbCS_3$) will be precipitated exclusively, and the corresponding potentiometric titration curve will consequently have only one step, as we have found (Fig. 4*a*). A titration curve with a single step is also obtained (ideally) when Ag^+ ions are added to a solution of sodium trithiocarbonate, but in this case the equivalence point denotes completion of the alternative reaction:

$$HS^- + [HCOS_2^-] + 2Ag^+ \longrightarrow Ag_2S + CS_2 + H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

We believe that this reaction occurs because the solubility product of silver hydrogen sulphide is less than that of silver trithiocarbonate (which is appreciably soluble, unlike Tl_2CS_3 or $PbCS_3$), and we consider that the mechanism of (7) must be as follows:

$$2HS^- + 2Ag^+ \longrightarrow [2AgSH] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$
$$[2AgSH] \rightleftharpoons Ag_2S + H_2S \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7b)$$
$$H_2S + 2Ag^+ \longrightarrow Ag_2S + 2H^+ \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7c)$$
$$2[HCOS_2^-] + 2H^+ \longrightarrow 2CS_2 + 2H_2O \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7d)$$

This conception of the reaction between silver ions and a solution of sodium trithiocarbonate is based primarily on our experience that, when it is followed potentiometrically, the amount of silver ions required is almost always less than expected and (paradoxically) a titration curve with *two* steps is usually obtained (Fig. 3*b*). These observations are highly significant, and we shall now show that both are consistent with the above mechanism.

It is reasonable to imagine that reaction (7) would yield a potentiometric titration curve of the same form (*i.e.*, with one step only) as that given by the analogous reaction between silver ions and a solution containing HS^- and HCO_3^- ions in equimolar concentrations. In seeking to explain why reaction (7) usually gives a two-step titration curve, we have been led to conclude that hydrogen ions react faster with the $HCOS_2^-$ ion than with the HS^- ion. Consequently, since atmospheric carbon dioxide is absorbed rapidly by solid sodium trithiocarbonate (which, of course, is exceedingly hygroscopic) and by its aqueous solutions, it is difficult in practice to avoid premature decomposition of a (small) proportion of the $HCOS_2^-$ ions produced in accordance with equation (6). Thus there will often be an excess of HS^- ions in a solution of sodium trithiocarbonate, and when there is it follows that reactions (7*a*), (7*b*), and (7*c*) will continue after (7*d*) has stopped. And so we can predict that in practice the termination of reaction (7) will tend to be the reaction between Ag^+ ions and HS^- ions which, as we have found, yields a characteristic two-step titration curve (Fig. 3*a*). This also explains why the titration curve of reaction (7), as it is usually observed (Fig. 3*b*), is simulated so remarkably well (though in respect of shape only) by the two-step curve that is obtained when silver ions are added to a solution of NaSH and $NaHCO_3$ in which the HS^- ions preponderate (Fig. 3*c*).

It is now obvious that, whenever a quantitative study of reaction (7) is undertaken, it is necessary to prevent an exchange of gases between the reaction mixture and the atmosphere. For if carbon dioxide enters the mixture, both HS^- and $HCOS_2^-$ ions will be destroyed (the latter preferentially) and, of course, oxygen also will reduce the concentrations of HS^- ions ($2HS^- \longrightarrow S_2^{2-} \longrightarrow S_2O_3^{2-}$). The absorption of carbon dioxide and oxygen from the air can be greatly reduced, if not prevented, by covering the mixture with a layer of toluene, but this does not always impede the escape of hydrogen sulphide sufficiently. Evidently, if part of the H_2S produced by reaction (7*b*) is lost, the quantity of H^+ ions produced by (7*c*) will be insufficient for (7*d*) and, consequently, some $HCOS_2^-$ ions will remain. It might be thought that, in the absence of hydrogen ions, these residual anions would combine with Ag^+ ions (the total consumption of Ag^+ ions would then be exactly equivalent to the original amount of sodium trithiocarbonate), but we consider that this does not happen because the available evidence suggests that $AgHCOS_2$ is almost completely dissociated in aqueous solution. (We have been unable to detect combination between Ag^+ ions and HCO_3^- ions potentiometrically or otherwise and, of course, neither $AgHCO_3$ nor $AgHCOS_2$ has been isolated.) Thus it follows that, if hydrogen sulphide is allowed to escape, the consumption of Ag^+ ions in reaction (7*c*) will be reduced, while if oxygen or carbon dioxide is allowed to enter the reaction mixture, less Ag^+ ions will be required in both (7*a*) and (7*c*). For these reasons, the estimation of sodium trithiocarbonate in aqueous solution by direct titration with standard silver nitrate solution may be expected to be inaccurate or unreliable (as we have found) unless very stringent precautions are taken. [In our experience it is both simplest and best to titrate a trithiocarbonate solution with standard acid (with care to exclude oxygen and carbon dioxide), or to decompose the salt with acid and collect the hydrogen sulphide evolved (weighed as PbS or, after oxidation, as $BaSO_4$). Alternatively, a spectrophotometric method may be used, with appropriate precautions.]

Our contention that the equilibrium $CS_3^{2-} + H_2O \rightleftharpoons [HCOS_2^-] + HS^-$ prevails in solutions of sodium trithiocarbonate is supported by other experimental evidence. For instance, we have found that, provided a trace of carbon disulphide is present initially,

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aniline reacts with sodium trithiocarbonate in aqueous solution to yield sodium phenyldithiocarbamate:

$$Ph{\cdot}NH_2 + CS_3^{2-} \longrightarrow S{:}C(NHPh){\cdot}S^- + HS^- \quad . . . . . (8)$$

This reaction, which occurs at room temperature, may be interpreted as follows:

$$Ph{\cdot}NH_2 + CS_2 \rightleftharpoons S{:}C(NHPh){\cdot}SH$$

$$CS_3^{2-} + H_2O \rightleftharpoons [HCOS_2^-] + HS^-$$

$$S{:}C(NHPh){\cdot}SH + [HCOS_2^-] \longrightarrow S{:}C(NHPh){\cdot}S^- + H_2O + CS_2$$

According to this mechanism, and in agreement with our observations, reaction (8) requires to be initiated by carbon disulphide but is thereafter a self-sustaining reaction. We added the necessary trace of carbon disulphide to the reaction mixture, but obviously it could be introduced, alternatively, by decomposing some $HCOS_2^-$ ions (*e.g.*, by allowing the trithiocarbonate solution to absorb sufficient atmospheric carbon dioxide beforehand).

Then, too, there is the method of preparing sodium tetrathiopercarbonate by adding elementary sulphur to a solution of the trithiocarbonate: $CS_3^{2-} + S \rightleftharpoons CS_4^{2-}$. This reaction, investigated by Gélis [20] and Yeoman,[5] can now be represented in terms of known reactions between sulphur and a solution of sodium hydrogen sulphide and between carbon disulphide and sodium disulphide:

$$CS_3^{2-} + H_2O \rightleftharpoons [HCOS_2^-] + HS^-$$

$$\begin{cases} HS^- + S \rightleftharpoons S_2^{2-} + H^+ \\ [HCOS_2^-] + H^+ \longrightarrow H_2O + CS_2 \end{cases}$$

$$CS_2 + S_2^{2-} \rightleftharpoons CS_4^{2-}$$

In order to summarize and correlate the conclusions we have reached so far about the hydrolysis of sodium trithiocarbonate, we assemble relevant equilibria as follows:

$$CS_3^{2-} \underset{HO^-}{\overset{H^+}{\rightleftharpoons}} HCS_3^- \underset{HS^-}{\rightleftharpoons} CS_2 \underset{HO^-}{\overset{HO^-}{\rightleftharpoons}} HCOS_2^- \underset{H^+}{\overset{HO^-}{\rightleftharpoons}} COS_2^{2-}\ (?)$$

$$HCS_3^- \overset{HO^-}{\rightleftharpoons} \left[\begin{matrix} HO & & S^{2-} \\ & C & \\ HS & & S \end{matrix}\right] \overset{HS^-}{\rightleftharpoons} HCOS_2^-$$

This system of equilibria includes the key equations (1), (4), (5), (5*a*), (5*b*), and (6), and is a substantial part of the comprehensive reaction scheme displayed on p. 4336.

It is now possible to discuss the further decomposition of the CS_3^{2-} ion which occurs when sodium trithiocarbonate is dissolved in water, or in aqueous sodium hydroxide solution, and the solution is heated for some time at about 90° in a sealed vessel. If sodium hydroxide is present, the trithiocarbonate is eventually converted, almost quantitatively, into carbonate and sulphide:

$$CS_3^{2-} + 6HO^- \longrightarrow CO_3^{2-} + 3S^- + 3H_2O \quad . . . . . (9)$$

We consider that this reaction depends primarily upon the hydrolysis of the CS_3^{2-} ion and proceeds as follows:

$$CS_3^{2-} + H_2O \rightleftharpoons [HCS_3^-] + HO^- \rightleftharpoons \left[\begin{matrix} HO & & S \\ & C & \\ HS & & S \end{matrix}\right]^{2-} \rightleftharpoons [HCOS_2^-] + HS^-$$

$$\left[\begin{matrix} HS & & O \\ & C & \\ HS & & S \end{matrix}\right]^{2-} \rightleftharpoons COS + 2HS^- \quad . (9a)$$

$$COS + HO^- \rightleftharpoons CO_2 + HS^- \quad . . . . . (9b)$$

$$CO_2 + 2HO^- \rightleftharpoons HCO_3^- + HO^- \rightleftharpoons CO_3^{2-} + H_2O \quad . . . (9c)$$

$$3HS^- + 3HO^- \rightleftharpoons 3S^{2-} + 3H_2O \quad . . . . . (9d)$$

[20] Gélis, *Compt. rend.*, 1875, **81**, 282.

Reaction (9*a*) includes (4) and (5*b*), and assumes a proton-shift within the hypothetical ortho-ion. Evidently, a high concentration of HO^- ions will favour the forward reaction in each of the conventional equilibria (9*b*), (9*c*), (9*d*), and the back-reaction of equation (4). Thus the rate of reaction (9) will not be a simple function of the concentration of hydroxyl ions and, in fact, we have observed that, at constant temperature (25°), the rate varies inversely with $[HO^-]$. This explains why the CS_3^{2-} ion is more stable in sodium hydroxide solution than in water.

It is reasonable to suppose that (9*a*) remains valid when the decomposition of the trithiocarbonate ion is caused by water alone but, under these conditions, HO^- ions can only be obtained by hydrolysis of HS^- ions ($HS^- + H_2O \rightleftharpoons HO^- + H_2S$) and so (9*b*)—(9*d*) must be modified appropriately. We thus postulate the following mechanism:

$$CS_3^{2-} + H_2O \rightleftharpoons COS + 2HS^- \quad \ldots\ldots\ldots \quad (9a)$$

$$2HS^- + 2H_2O \rightleftharpoons 2H_2S + 2HO^-$$

$$COS + 2HO^- \rightleftharpoons HCO_3^- + HS^- \rightleftharpoons CO_3^{2-} + H_2S$$

That is,

$$CS_3^{2-} + 3H_2O \rightleftharpoons CO_3^{2-} + 3H_2S \quad \ldots\ldots\ldots \quad (10)$$

It will obviously be very difficult in practice to achieve total decomposition of the trithiocarbonate ion in accordance with (10), but the above mechanism implies that, if equilibrium is established under particular conditions, it should be possible to demonstrate that the reaction mixture then contains carbonate (HCO_3^-, CO_3^{2-}) and sulphide (HS^-, H_2S) in the molar ratio 1 : 3. We find that this is the case, and, under our experimental conditions, approximately 0·5 mole of carbonate and 1·5 moles of sulphide were obtained from 1 mole of sodium trithiocarbonate (cf. Yeoman [5]).

The mechanism which we have proposed for reaction (9*a*) is consistent with our observations of the changes which occur in the absorption spectrum of a solution of sodium trithiocarbonate in contact with air (at room temperature): two well-defined bands with their peaks at 308 and 378 mμ always develop (Fig. 1), rapidly in a dilute aqueous solution of the salt and slowly if sodium hydroxide is present. This unique spectrum (which, significantly, is not observed in solutions of sodium ethyl xanthate) is easily distinguishable from that given by solutions of sodium tetrathiopercarbonate, Na_2CS_4, and we suggest that it should be assigned to the trithiopercarbonate ion, COS_3^{2-}, which could well be produced by oxidation of one of the ortho-ions involved in (9*a*):

$$[CH_2OS_3]^{2-} \xrightarrow{O} COS_3^{2-} + H_2O$$

To test this hypothesis we saturated 1% solutions of both sodium hydrogen sulphide and sodium sulphide with carbon oxysulphide and then with oxygen (after which they were kept overnight at room temperature) in order to see if the following predictable reactions could be realized:

$$COS + 2HS^- \longrightarrow \left[\begin{matrix} HS \\ HS \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} O \\ S \end{matrix}\right]^{2-} \xrightarrow{O} COS_3^{2-} + H_2O$$

Immediately after they had been treated the solutions gave two absorption bands with peaks at 320 and 400 mμ (these bands had different relative intensities from those produced by the CS_4^{2-} ion, and we have assigned them provisionally to the ortho-ion); but, when sufficient oxidation had occurred, these bands had disappeared and were replaced by another pair of bands with their peaks at 308 and 378 mμ respectively and with relative intensities similar to those of the tetrathiopercarbonate bands. These new bands were

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indistinguishable from those previously observed in old (*i.e.*, oxidised) solutions of sodium trithiocarbonate (Fig. 1*c*).

Reactions in Ethanolic Solutions.—We have shown that when sodium trithiocarbonate is dissolved in ethanol, sodium ethyl xanthate and sodium hydrogen sulphide are produced:

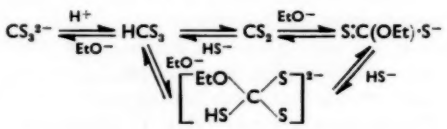
$$Na_2CS_3 + EtOH \rightleftharpoons S{:}C(OEt){\cdot}SNa + NaSH \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

We have also found that analogous reactions occur when the salt is dissolved in methanol, propanol, ethylene glycol, and glycerol. So far as we know, none of these reactions has been reported previously.

An investigation of reaction (11) has shown that if the concentration of sodium trithiocarbonate is small (*ca.* 1%), and the reaction proceeds at 25°, then the yield of sodium ethyl xanthate reaches 90% of the maximum yield in about 6 hr., irrespective of whether anhydrous or hydrated trithiocarbonate is used. Moreover, in a crucial experiment, in which water and air were excluded from the system, anhydrous sodium trithiocarbonate reacted readily with anhydrous ethanol at room temperature. On this evidence we conclude that the two compounds combine without prior hydrolysis of the trithiocarbonate, and we consider that the reaction depends, primarily, on the transference of a proton from ethanol to the CS_3^{2-} ion:

$$CS_3^{2-} + EtOH \rightleftharpoons [HCS_3^-] + EtO^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

In other words, we believe that the reactions of sodium trithiocarbonate with ethanol and with water are analogous. Hence, by following the pattern of hydrolysis [see equations (5), (5*a*), (5*b*)], we can formulate, tentatively, the following system of equilibria pertaining to ethanolic solution:



This scheme affords two possible mechanisms for (11): one of these includes the well-known reaction $CS_2 + EtO^- \rightleftharpoons S{:}C(OEt){\cdot}S^-$ and is in that respect more plausible than the other, which depends on the formation of a hypothetical intermediate ortho-ion. The scheme also enables the decomposition of sodium trithiocarbonate in ethanolic solution by carbon dioxide or hydrogen sulphide to be explained:

$$CS_3^{2-} + EtOH \rightleftharpoons [HCS_3^-] + EtO^-$$

$$[HCS_3^-] \rightleftharpoons CS_2 + HS^-$$

$$2(CO_2 + EtOH \rightleftharpoons EtCO_3^- + H^+)$$

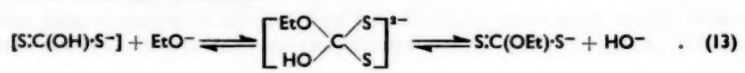
or

$$2(H_2S \rightleftharpoons HS^- + H^+)$$

$$EtO^- + HS^- + 2H^+ \longrightarrow EtOH + H_2S$$

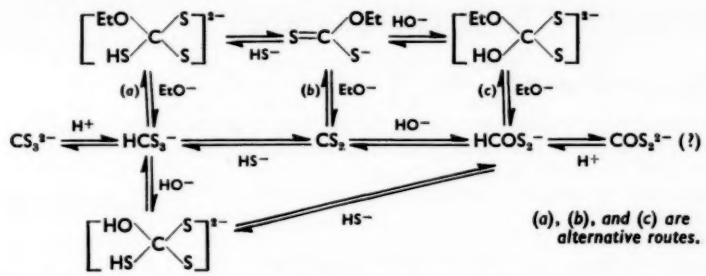
It is seen that the decomposition of 1 mole of Na_2CS_3 should yield 2 moles of $NaEtCO_3$ or NaSH, as we have found.

If sodium trithiocarbonate is dissolved in a mixture of ethanol and water, there will obviously be competition between ethanolysis and hydrolysis, and this might well provide a third route to sodium ethyl xanthate:



(13)

In this event, the equilibria in an aqueous ethanolic solution of sodium trithiocarbonate could be envisaged as follows:



Formation of Sodium Trithiocarbonate.—We have shown how crystalline $Na_2CS_3,2H_2O$ and amorphous Na_2CS_3 can be obtained reproducibly by the action of carbon disulphide on an aqueous solution of either sodium sulphide or sodium hydroxide. We also isolated crystalline tri- and tetra-hydrates, but we did not obtain the monohydrate described by Yeoman.[5]

Anhydrous sodium trithiocarbonate and the dihydrate are exceedingly hygroscopic and, when moist, react rapidly with atmospheric carbon dioxide and oxygen, after hydrolysis of the CS_3^{2-} ion. Thus it is not easy to preserve this salt in a state of purity or to carry out exact quantitative work with it. The dried salt can be preserved *in vacuo*, or in dry nitrogen, or under liquid carbon disulphide, but we found it best to use fresh material whenever possible. By working quickly it is practicable to handle the salt in the open (as we did) but, for some purposes, it would be advantageous to employ a " glove-box " filled with dry nitrogen.

The reaction between carbon disulphide and an aqueous solution of sodium sulphide (or moist crystals of $Na_2S,9H_2O$) can be represented as follows:

$$S^{2-} + H_2O \rightleftharpoons HO^- + HS^-$$

$$CS_2 + HS^- \rightleftharpoons [HCS_3^-]$$

$$[HCS_3^-] + HO^- \rightleftharpoons CS_3^{2-} + H_2O$$

That is,

$$CS_2 + S^{2-} \rightleftharpoons CS_3^{2-} \quad \ldots\ldots\ldots\ldots \quad (14)$$

It is reasonable to assume an analogous reaction when sodium trithiocarbonate is prepared by adding carbon disulphide to a solution of sodium ethoxide in dry ethanol which has been saturated with dry hydrogen sulphide: [5]

$$EtO^- + H_2S \rightleftharpoons EtOH + HS^-$$

$$CS_2 + HS^- \rightleftharpoons [HCS_3^-]$$

$$[HCS_3^-] + EtO^- \rightleftharpoons CS_3^{2-} + EtOH$$

In this case the loss of trithiocarbonate caused by its conversion into sodium ethyl xanthate [$CS_3^{2-} + EtOH \rightleftharpoons S{:}C(OEt){\cdot}S^- + HS^-$] can obviously be reduced by maintaining a high concentration of HS^- ions but, of course, it may then be difficult to obtain sodium trithiocarbonate entirely free from sodium hydrogen sulphide.

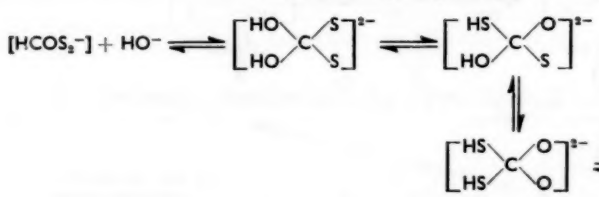
The reaction between carbon disulphide and an aqueous solution of sodium hydroxide must occur in at least two stages since HS^- ions are needed for the formation of CS_3^{2-} ions. In agreement with other workers,[21] we assume the first stage to be:

$$CS_2 + 6HO^- \longrightarrow 2S^{2-} + CO_3^{2-} + 3H_2O \quad \ldots\ldots\ldots \quad (15)$$

[21] Cherkasskaya, Pakshver, and Kargin, *J. Appl. Chem.* (*U.S.S.R.*) (U.S. translation), 1953, **26**, 55.

and we consider that this reaction (which completes the comprehensive scheme presented on p. 4336) might proceed as follows:

$$CS_2 + HO^- \rightleftharpoons [HCOS_2^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$



$$CO_2 + 2HS^- \quad (15b)$$

$$CO_2 + 2HO^- \longrightarrow CO_3^{2-} + H_2O$$

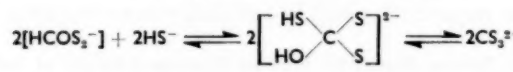
$$2HS^- + 2HO^- \longrightarrow 2S^{2-} + 2H_2O$$

Evidently, if (15) were followed by $CS_2 + S^{2-} \longrightarrow CS_3^{2-}$ [see (14)], sodium trithiocarbonate would be produced in accordance with the classic equation $3CS_2 + 6HO^- \longrightarrow 2CS_3^{2-} + CO_3^{2-} + 3H_2O$ (Berzelius). But the Berzelius equation would also be satisfied if the reaction followed an alternative route (as is indicated in the comprehensive scheme):

$$3CS_2 + 3HO^- \rightleftharpoons 3[HCOS_2^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

$$[HCOS_2^-] + HO^- \rightleftharpoons CO_2 + 2HS^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15b)$$

$$CO_2 + 2HO^- \longrightarrow CO_3^{2-} + H_2O$$



$$2CS_3^{2-} + 2H_2O \quad . \quad . \quad . \quad (15c)$$

The latter mechanism has the merit that it suggests the possibility of isolating a product (disodium dihydrogen trithio-orthocarbonate monohydrate, $Na_2H_2COS_3,H_2O$) which might be expected to differ physically, though not chemically, from disodium trithiometacarbonate dihydrate, $Na_2CS_3,2H_2O$, which is commonly thought to be given by the reaction (14). This is of interest because we always obtained different kinds of crystals (needles, plates) by our two methods of preparing sodium trithiocarbonate, and whenever either product was recrystallized, only plates were produced. It is at least possible that the needles and plates were $Na_2H_2COS_3,H_2O$ and $Na_2CS_3,2H_2O$, respectively, and it would not be surprising if the ortho-salt were metastable and hence could be isolated only from the original mother-liquor (which presumably contained various anions, including HO^-).

Finally, it may be noted that if the back-reaction of (14) were followed by (15), the resulting decomposition of the CS_3^{2-} ion would still satisfy equation (9). The available experimental evidence does not indicate how important this mechanism might be in comparison with that represented by equation (9*a*) but, as we have seen, the latter reaction always occurs, even when the concentration of hydroxyl ions is small and there is consequently appreciable hydrolysis of the CS_3^{2-} ion. We consider that the decomposition of trithiocarbonate by HO^- ions normally proceeds by both routes simultaneously, as is indicated in the comprehensive scheme (p. 4336).

We are grateful to D. A. Taylor for his assistance throughout this investigation, and to (Mrs.) G. Hancock and M. Lonsdale for estimating carbon and hydrogen in sundry specimens. We are also indebted to several of our colleagues for their comments and advice on various aspects of the work.

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[*Received, May 6th*, 1957.]

869. *Addition Compounds of Gallium Trichloride. Part IV.* The Thermal Stability and Heat of Formation of Gallium Trichloride–Phosphorus Trichloride.*

By N. N. Greenwood, P. G. Perkins, and K. Wade.

Gallium trichloride and phosphorus trichloride form a 1 : 1 addition compound which melts incongruently at 28°. The heat of the reaction is 3·4 kcal. mole^{-1} at 25°; this corresponds to a heat of formation from the elements of 203·2 kcal. mole^{-1} for the equilibrium mixture of crystalline complex in the presence of its liquid dissociation products. The absence of any appreciable electrical conductivity in the system is interpreted in terms of an "ethane-like" structure $Cl_3Ga \leftarrow PCl_3$ for the complex which dissociates in the liquid state to give a solution of Ga_2Cl_6 in PCl_3.

The only recorded compounds in which phosphorus, arsenic, or antimony forms a direct donor–acceptor bond to gallium are the methyl derivatives Me_3Ga,XMe_3 (X = P, As, Sb).[1] Considerable interest attaches to such compounds because they afford a means of studying the interplay of several factors on bond strength and on the tendency to ionise. For example, the complex $Me_3Ga,AsMe_3$ (m. p. 23·5°) [1] may owe part of its stability to the heteropolarity of the Ga–As bond, since it is isoelectronic with the unknown hexamethyldigermane Ge_2Me_6 (though it is not certain that hexamethyldigermane could not be prepared, for the hexaethyl derivative is a stable compound). The possibility of interaction between the trihalides of these elements introduces a further factor, for the gallium trihalides, unlike trimethylgallium, are dimeric and the formation of an adduct involves the preliminary breaking of two halogen bridge bonds with consequent reduction in stability. Thus, despite the existence of hexachlorodisilane (Si_2Cl_6) there is no interaction between aluminium trichloride (Al_2Cl_6) and phosphorus trichloride to give the isoelectronic complex $AlCl_3,PCl_3$. However, replacement of aluminium trichloride by gallium trichloride increases the disparity in electropositivity of the donor and acceptor atoms and also lowers the dimerisation energy of the acceptor molecule, thus permitting the formation of an unstable complex $GaCl_3,PCl_3$. The present work was undertaken to investigate whether this complex has an ethane-like structure with a covalent Ga–P bond, or whether the difference in electropositivity of gallium and phosphous was sufficient to result in an ionic complex such as aluminium tribromide–antimony tribromide.[2]

Experimental and Results

Phosphorus trichloride was purified by fractionation in a 50-cm. column packed with glass helices and was handled thereafter in a vacuum line. Gallium trichloride was prepared and purified as described in Part I [3] which also outlined the techniques used to obtain the melting-point data. The heat of reaction was determined by use of the calorimeter described in Part III.[4] The circuit used to measure the electrical conductivity at 1000 cycles/sec. has also been described previously.[5]

When successive amounts of phosphorus trichloride are distilled on to gallium trichloride, the m. p. of the system drops steadily as indicated in Table 1. The results are plotted in the Figure which shows the presence of a 1 : 1 addition compound melting incongruently at 28°.

The heat of reaction of 1 mole of crystalline gallium trichloride with one mole of liquid phosphorus trichloride to give a two-phase mixture of solid addition compound in equilibrium

* The paper, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291, is regarded as Part III.

[1] Coates, *J.*, 1951, 2003.

[2] Isbekow, *Z. anorg. Chem.*, 1926, **158**, 87; Gorenbein, *Zhur. obshchei Khim.*, 1948, **18**, 1427, and refs. therein.

[3] Greenwood and Wade, *J.*, 1956, 1527.

[4] Greenwood and Perkins, *J. Inorg. Nuclear Chem.*, 1957, **4**, 291.

[5] Greenwood and Worrall, *ibid.*, 1957, **3**, 357.

TABLE 1. *Melting point of the system gallium trichloride–phosphorus trichloride.*

PCl_3 (mole %)	0·0	1·5	5·8	9·1	12·3	17·4	21·8	24·5	29·9	33·7	37·5	41·5	44·6
M. p.	77·8°	77·2°	75°	72·5°	70·5°	67°	63·5°	60°	55·5°	52°	47°	42°	38·5°
PCl_3 (mole %)	47·4	49·7	54·1	57·0	58·9	61·4	65·3	69·1	75·9	83·8	86·6		100·0
M. p.	34°	32°	27°	25·5°	23°	20°	16°	11°	1·5°	−13·5° *	−21·5° *		−90°

* and a eutectic at −93°.

with its liquid dissociation products at 25° was obtained from the heats of solution of gallium trichloride and of the complex in phosphorus trichloride:

$$GaCl_3(c) + (x + 1)PCl_3(l) = GaCl_3,PCl_3 \text{ (in excess of } PCl_3); \quad -\Delta H = 12{\cdot}9 \text{ kcal. mole}^{-1}$$

$$GaCl_3,PCl_3(2\text{-phase}) + xPCl_3(l) = GaCl_3,PCl_3 \text{ (in excess of } PCl_3); \quad -\Delta H = 9{\cdot}5 \text{ kcal. mole}^{-1}$$

$$\text{Therefore, } GaCl_3(c) + PCl_3(l) = GaCl_3,PCl_3(2\text{-phase}); \quad -\Delta H = 3{\cdot}4 \text{ kcal. mole}^{-1}$$

The supporting thermochemical data are presented in Tables 2 and 3. It should perhaps be emphasised that the precise chemical constitution of the final state in the solution reactions is

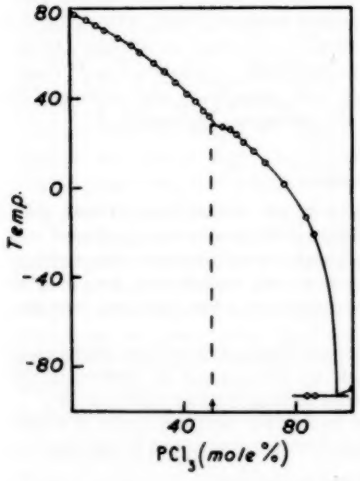
TABLE 2. $GaCl_3$ (c) + *excess of* PCl_3 (l) = $GaCl_3,PCl_3$ (*in excess of* PCl_3).

PCl_3 (g.)	$GaCl_3$ (g.)	Mole ratio	ΔT(μV)	Calibration (cal. per μV)	$-\Delta H$ (kcal. mole^{-1})
150 g.	0·0713	2700 : 1	69·0	0·0759	$12{\cdot}9_5$
150 g.	0·0668	2880 : 1	66·0	0·0742	$12{\cdot}9_2$
				Mean	$12{\cdot}9_4$

TABLE 3. $GaCl_3,PCl_3$ (2-*phase*) + *excess of* PCl_3(l) = $GaCl_3,PCl_3$ (*in excess of* PCl_3).

PCl_3 (g.)	$GaCl_3,PCl_3$ (g.)	Mole ratio	ΔT(μV)	Calibration (cal. per μV)	$-\Delta H$ (kcal. mole^{-1})
190 g.	0·2484	1740 : 1	89·0	0·0853	$9{\cdot}5_5$
192 g.	0·7724	567 : 1	264·0	0·0892	$9{\cdot}5_3$
				Mean	$9{\cdot}5_4$

immaterial provided that it is the same for both reactions so that Hess's law can be applied. It has been specified in the equations as " $GaCl_3,PCl_3$ (in excess of PCl_3) " for convenience but it might equally well have been written as " $\frac{1}{2}Ga_2Cl_6$ in $(x + 1)PCl_3$ " or even non-committally as " final state."



DISCUSSION

The very small value (3·4 kcal. mole^{-1}) for the interaction of gallium trichloride with phosphorus trichloride at 25° implies that the complex is unstable with respect to dissociation into its donor and acceptor components, for the decrease in entropy during the reaction might reasonably be expected to be about 10—15 cal. deg.$^{-1}$ mole^{-1}, so that the free-energy change ($-\Delta G = -\Delta H + T\Delta S = 3400 - 300|\Delta S|$) would be approximately zero or slightly negative, implying a fairly evenly balanced equilibrium between the complex and its components.

The standard heat of formation of the equilibrium mixture containing the dissociating incongruent compound can be estimated from the known heats of formation of $GaCl_3$(c) [6] and PCl_3(l); [7] these are 125·4 and 74·4 kcal. mole^{-1} respectively and lead to a value of $-\Delta H_f^\circ$ ($GaCl_3,PCl_3$: two-phase) = 203·2 kcal. mole^{-1}. There is little point in trying to

[6] Klemm and Jacobi, *Z. anorg. Chem.*, 1932, **207**, 177.
[7] Neale and Williams, *J.*, 1954, 2156.

evaluate the corresponding heat for the gas-phase reaction since the complex is completely dissociated even in the liquid phase.

The simplest structure for the solid complex gallium trichloride–phosphorus trichloride is the ethane-like model $Cl_3Ga \leftarrow PCl_3$. The only comparable compound containing a gallium–phosphorus bond is $Me_3Ga \leftarrow PMe_3$; this melts at 56·5° and has an extrapolated b. p. of 173°.[1] Its greater stability is indicated by the fact that it is less than 10% dissociated in the vapour phase at 100° and has a heat of dissociation of 18 kcal. mole^{-1}. The incongruent melting point of the chlorine derivative implies complete dissociation in the liquid phase at room temperature. This is confirmed by a preliminary investigation of the Raman spectra carried out in collaboration with Dr. L. A. Woodward and Mr. R. Taylor, who found, qualitatively, that only the lines of the parent species Ga_2Cl_6 and PCl_3 were present in a solution of approximate composition $GaCl_3 + 2PCl_3$.

Absence of any appreciable ionic dissociation in the system was demonstrated by measurement of the electrical conductivity of a 1 : 1 mixture of the components prepared by the vacuum-line techniques previously described.[8] At 25°, the specific conductivity was $2{\cdot}87 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ and this increased as the temperature was raised in the range up to 75° with an activation energy for conduction of about 6 kcal. mole^{-1}. Partial freezing of the complex decreased the conductivity more than twofold. The conductivity of phosphorus trichloride was $< 4 \times 10^{-8}$ ohm^{-1} cm.$^{-1}$; that of gallium trichloride is $1{\cdot}86 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$ at 78°.[5]

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THE UNIVERSITY, NOTTINGHAM. [*Received, June 5th,* 1957.]

[8] Greenwood and Wade, *J.*, 1957, 1516.

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870. *Quantitative Aspects of Reductions of Carbohydrates by Potassium Borohydride.*

By P. D. BRAGG and L. HOUGH.

Estimations of the uptake of hydrogen from borohydride in borate buffer, by various monosaccharides and their derivatives, have shown that 3-*O*-substituted aldoses and 4-*O*-substituted hexuloses react slowly because of steric hindrance. Smaller but significant differences in reaction rates have been attributed to the formation of borate complexes.

REDUCTION by borohydride has been utilised for quantitative semimicro-estimation of monosaccharides and reducing oligosaccharides by determining the consumption of hydrogen,[1-3] and also of oligosaccharides by colorimetric estimation of the carbohydrate before and after reduction.[4] We have studied the rate of reduction of various reducing carbohydrates, using Lindberg and Theander's procedure,[1,2] but with an improved apparatus. The reductions were in aqueous borate buffer at pH 10·3, which has been found optimum for this reaction.[2,5]

In the presence of excess of borohydride, the conversion of aldoses into glycitols [6] is generally accepted as being complete within a few hours. However, determinations of the rates of reduction of various mono- and di-saccharides have revealed that, under the

[1] Lindberg and Missiorny, *Svensk. Papperstidning*, 1952, **55**, 13.
[2] Lindberg and Theander, *ibid.*, 1954, **57**, 83.
[3] Skell and Crist, *Nature*, 1954, **173**, 401.
[4] Peat, Whelan, and Roberts, *J.*, 1956, 2258.
[5] Head, *Shirley Institute Memoirs*, 1955, **28**; *J. Text. Inst.*, 1955, **46**, T 400.
[6] Abdel-Akher, Hamilton, and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4691.

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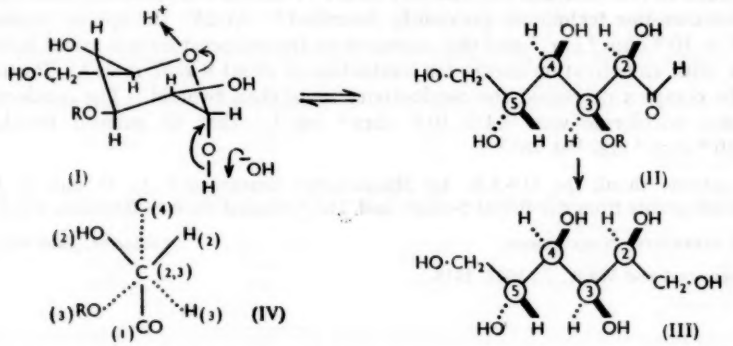
conditions described herein, whilst the majority (Table 1; group A) were reduced stoicheiometrically within 1—2 hr., there were exceptions (Table 1; group B) which required at least 6 hr. for complete reduction. Of the aldoses studied, only those with a 3-*O*-substituent fell into group B (see Table 1), namely, 3-*O*-methyl-D-glucose (I; R = OMe), laminaribiose (I; R = β-D-glucopyranosyl), 2 : 3 : 4 : 6-tetra-*O*-methyl-D-glucose, and 2 : 3 : 4 : 6-tetra-*O*-methyl-D-galactose. These results were confirmed by following the changes in the amounts of formaldehyde produced on periodate oxidation of mixtures of aldoses and borohydride.[7]

The reduction of an aldose (*e.g.*, I) to a glycitol (*e.g.*, III) will be preceded by ring-opening of the cyclic modification (I) of the aldose to the *aldehydo*-form in the acyclic staggered zig-zag conformation (II).[8,9] These results are consistent with the view that a bulky substituent at $C_{(3)}$ of this conformation (II) causes the approach of a borohydride ion to the aldehyde group to be sterically hindered (see the projection along the $C_{(2)}$–$C_{(3)}$ bond; IV). Thus 3-*O*-methyl-D-glucose (I; R = OMe) reacted more rapidly with borohydride than laminaribiose (I; R = β-D-glucopyranosyl) with its more bulky substituent at $C_{(3)}$. Under the same conditions laminarin, a polysaccharide containing β-1 : 3-D-glucopyranosyl units, did not consume any measurable amount of borohydride.



Nevertheless, in group A there were small but distinct differences in the rates of reaction which must be attributed to other stereochemical factors involving the conformations of the cyclic modifications of the aldoses and the stability of derived borate complexes.[10–12] The formation of borate complexes which involve substitution at either $C_{(1)}$ or $C_{(3)}$ of the open-chain forms should also reduce the rate of reduction, but in view of the following results is not considered to be of importance. Acetaldehyde, D-glyceraldehyde, 4 : 6-*O*-ethylidene-D-glucose, and 2-deoxy-D-glucose were more rapidly reduced (<15 min.) than D-xylose (30 min.) and D-glucose (1 hr.). These observations are in accord with previous results[10,11,13,14] on borate-complex formation with various derivatives of D-glucose and suggest that D-xylose and D-glucose form fairly stable borate complexes in their furanose forms at $C_{(1)}$ and $C_{(2)}$. Böeseken[13] has shown that the strongest boric acid complex formation occurs with true *cis*-glycols which are found in the furanose forms of monosaccharides but not in the pyranosides in their chair conformations. In the case of D-glucose, all its free hydroxyls appear to be capable of borate-complex formation to a certain extent,[11] which probably accounts for its slower reaction than that of D-xylose.

[7] Hough, Perry, and Woods, *Chem. and Ind.*, 1957, 1100.
[8] Barker, Bourne, and Whiffen, *J.*, 1952, 3865.
[9] Barton and Cookson, *Quart. Rev.*, 1956, **10**, 44.
[10] Foster, *J.*, 1953, 982.
[11] Foster and Stacey, *J.*, 1955, 1778.
[12] Foster, *J.*, 1957, 1395.
[13] Böeseken, *Adv. Carbohydrate Chem.*, 1949, **4**, 189; *Rec. Trav. chim.*, 1921, **40**, 553.

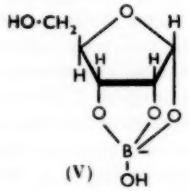
Cellobiose (4-*O*-β-D-glucopyranosyl-D-glucose), which cannot pass into the furanose form, was reduced more rapidly than melibiose (6-*O*-β-D-galactopyranosyl-D-glucose). The slower reaction of glucose than galactose and mannose can be correlated with the greater conformational stability of the 1 : 2-borate complex of glucofuranose which has fewer *endo*-groups than those derived from the latter hexoses.

Of the aldopentoses D-ribose behaved atypically, since L-arabinose, D-lyxose, and D-xylose were reduced at an appreciably faster rate. Since D-ribose exists in aqueous solution to an appreciable extent (10—30%) in the *aldehydo*-form whereas other aldopentoses do not (<1%),[15,16] it follows that in borate solution a relatively stable complex of D-ribose was formed. These results, the ready formation of 2 : 3-*O*-cyclic acetals of D-ribofuranose,[17] and the greater mobility during ionophoresis of D-ribofuranoside 5-phosphate than of the 2- and 3-phosphates,[18] suggested that this pentose may have reacted in the furanose form with borate at the true *cis*-hydroxyls at $C_{(1)}$, $C_{(2)}$, and $C_{(3)}$ to give a tridentate structure (V).[19] Angyal and McHugh [19] have found that certain cyclitols with borate form tridentate structures which are relatively strong acids containing a 1 : 1 ratio of borate to cyclitol. Using their procedure, we found ribose to depress the pH of a borate solution to a greater extent than other pentoses (Table 3), but calculation of the equilibrium constants for the formation of a tridentate complex did not give constant K values over a wide range of concentrations of pentose (Table 4). However, D-ribose, D-xylose, and L-arabinose followed approximately the equation $K = [C^-]/[B^-][P]^x$, where $x = 1{\cdot}84$, 1·84, and 1·90, respectively, indicating the presence of both 1 : 1 and 2 : 1 complexes [20] (Table 4) ($[C^-]$, $[B^-]$, and [P] are the concentrations of complex anion, borate ion, and pentose, respectively). Complex formation was more extensive with ribose ($K = 5{\cdot}14 \times 10^4$) than xylose ($K = ca.\ 4{\cdot}2 \times 10^3$) and arabinose ($K = 1{\cdot}73 \times 10^3$) which would suggest that the hydrolysis of the borate complex is a rate-determining step in the reduction by borohydride. We conclude that ribose reacts in the furanose form at $C_{(1)}$ and $C_{(2)}$ with borate, as also suggested by the behaviour of various methyl ethers of ribose during ionophoresis,[21] and that there is little, if any, tridentate formation. Measurement of the optical rotation of D-ribose in borate gave a constant value of +8·5° as compared with −19·8° found in aqueous solution, thus confirming that complexes had been formed. D-Glucose, D-mannose, D-galactose, and L-arabinose also showed changes (Table 2), but interpretation is complicated by the various types of borate complexes present in the equilibrium mixtures.[22]

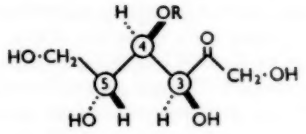
That ketoses were reduced more slowly than aldoses, was shown by comparing dihydroxyacetone with D-glyceraldehyde, and D-fructose with D-glucose and D-mannose. This difference is related to the increased steric hindrance of the carbonyl group in ketoses by neighbouring substituents, a conclusion supported by the slow consumption of borohydride by turanose (3-*O*-α-D-glucopyranosyl-D-fructose) compared with D-fructose. As noted by Peat, Whelan, and Roberts,[4] maltulose (4-*O*-α-D-glucopyranosyl-D-fructose) was resistant to reduction during 9 hr. The behaviour of maltulose thus paralleled that of 3-*O*-substituted aldoses and may be accounted for by the intermediary formation of the staggered zig-zag conformation (VI) in which the bulky substituent at $C_{(4)}$ interferes with the reduction at $C_{(2)}$. Amino- and acetamido-groups adjacent to the aldose carbonyl group had little influence on the rates of reduction as revealed by examining 2-amino- and 2-acetamido-2-deoxy-D-glucose; from the latter 2-acetamido-2-deoxy-D-glucitol was prepared *via* the penta-acetate.

[14] Lock and Richards, *J.*, 1955, 3024.
[15] Cantor and Peniston, *J. Amer. Chem. Soc.*, 1940, **62**, 2113.
[16] Overend, Peacocke, and Smith, *Chem. and Ind.*, 1957, 113.
[17] Jeanloz and Fletcher, *Adv. Carbohydrate Chem.*, 1951, **6**, 168.
[18] Burke and Foster, *Chem. and Ind.*, 1955, 94.
[19] Angyal and McHugh, *J.*, 1957, 1423.
[20] Antikainen, *Acta Chem. Scand.*, 1955, **9**, 1008.
[21] Brown, Magrath, and Todd, *J.*, 1954, 1442.
[22] Isbell, Brewster, Holt, and Frush, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 120.

The reduction of lactones to glycitols was incomplete (see Table 1; group C) owing to competing hydrolysis of the lactone to form non-reducible sodium salts.[23,24] Thus, L-gulono-1 → 4-lactone and D-glucofuranurono-6 → 3-lactone consumed *ca.* 0·6 mol. and *ca.* 2·0 mol. of hydrogen (constant values) respectively as compared with 2 mol. and 3 mol. required in theory. These results could also be interpreted by partial reduction



(V)



(VI)

of the lactones to intermediary aldoses,[23,25] but reducing substances were not found. High yields of glycitols from γ-lactones have been obtained in reductions in either acid medium or anhydrous methanol,[24] thus obviating hydrolysis.

Re-examination [4] of the borohydride reduction of lactose has shown that lactitol was formed in high yield and that the reductive fission previously indicated [26] was anomalous owing to the conditions [27] used for isolation of the product. In the previous investigation, sodium ions were removed from the mixture by ion exchange on Amberlite IR-120(H^+) resin, giving unexpectedly a strongly acidic solution, distillation of which with methanol caused methanolysis of the lactitol and formation of sorbitol and methyl glucosides.

Experimental

Method.—The reducing substance (*ca.* 200—300 mg.; accurately weighed) was dissolved in 0·1M-boric acid solution (25·0 ml.) and an aliquot portion (3·0 ml.) transferred into one of the two lower compartments of the reaction flask (50 ml.) (see Inset), which was designed for easy filling and mixing. Into the other compartment a 0·13M-solution (3·0 ml.) of potassium borohydride in 0·1N-sodium hydroxide was introduced. The side-arm of the flask was carefully charged with 10N-sulphuric acid (*ca.* 2 ml.). The vessel was then connected through a ground-glass joint (B.24) to a gas-burette (50 ml.) and the volume recorded before the boric acid and borohydride solutions were thoroughly mixed by tilting and gentle rotation of the apparatus. To minimise loss of hydrogen, the gas pressure in the apparatus was reduced to atmospheric pressure from time to time by altering the height of the water reservoir. If the evolution of hydrogen was slow, the reaction could be allowed to continue for 24 hr. without appreciable loss of hydrogen, but generally reduction times of a few hours were employed. After a suitable period, the reaction was stopped by tipping the acid from the side-arm into the solution. The total volume of hydrogen evolved was measured in the gas-burette after vigorous shaking had freed the solution of hydrogen. A blank containing no reducing substance was run concurrently with every determination. By difference, the amount of hydrogen consumed by the substance was obtained. All reactions were carried out at 22°. The accuracy of the determination was ±5%.

Effect of Borate on the Optical Rotation of Monosaccharides.—The optical rotations of the following monosaccharides were measured in water and in 0·1M-boric acid–0·1N-sodium hydroxide solution, a 1 dm. tube being used, until a constant value was obtained.

Determination of the Equilibrium Constants for the Pentose–Borate Reactions.—The determination was carried out in 0·0025M-sodium tetraborate by Angyal and McHugh's method.[19]

[23] Wolfrom and Wood, *J. Amer. Chem. Soc.*, 1951, **73**, 2933.
[24] Frush and Isbell, *ibid.*, 1956, **78**, 2844.
[25] Macdonald and Fischer, *ibid.*, p. 5025.
[26] Hough, Jones, and Richards, *Chem. and Ind.*, 1953, 1064.

TABLE 1. *Hydrogen uptake from borohydride (moles of* H_2 *per mole of substance).*

Substance	Wt. of sample (mg.)	Time of reduction: 5 (min.)	10 (min.)	15 (min.)	30 (min.)	60 (min.)	3 (hr.)	4 (hr.)	5 (hr.)	24 (hr.)
Group A										
Acetaldehyde	31·6	1·03	1·07			1·06 [c]				
DL-Glyceraldehyde	26·4	0·93	0·95	1·00	1·00					
D-Xylose	44·0	0·66	0·75	0·79	1·03	1·03				
D-Ribose	45·2			0·38	0·56	0·89		1·06		
L-Arabinose	39·5	0·74		0·94	1·05 [a]					
D-Lyxose	48·4	0·67	0·98	0·96	1·05					
D-Glucose	52·3			0·67	0·85 [b]	1·02	1·02			0·98
D-Mannose	51·7	0·38	0·68	0·81	0·98					
D-Galactose	59·0	0·46		0·79	0·96					
L-Rhamnose monohydrate	32·9					1·00	1·04			
2-Deoxy-D-glucose	51·9	0·88	1·00	1·00	1·01	1·04		1·03		
4 : 6-*O*-Ethylidene-D-glucose	21·9	0·98	1·04	1·04	1·04	1·05		1·04		
Cellobiose	60·2	0·47	0·71	0·85	1·02	0·96				1·01
Lactose monohydrate	47·7					0·98		0·98		1·06
Melibiose	61·5			0·59	0·73	0·98		0·94		
D-*glycero*-D-*galacto*-Heptose	24·7		0·78	0·88 (20 min.)	0·99	0·96				
2-Amino-2-deoxy-D-glucose	33·1					1·05	1·07			
2-Acetamido-2-deoxy-D-glucose	30·7					1·00		1·04		
Methyl α-D-glucoside	30·0									0·0
Dihydroxyacetone	25·1			0·84	0·90	1·00				
D-Fructose	54·4			0·54	0·78	0·95		1·02		1·02
Group B										
3-*O*-Methyl-D-glucose	18·5					0·28	0·38			0·94 [d]
										1·02
2 : 3 : 4 : 6-Tetra-*O*-methyl-D-glucose	28·4					0·27				
2 : 3 : 4 : 6-Tetra-*O*-methyl-D-galactose	15·3					0·53	0·69			0·97 [e]
Laminaribiose	8·3					0·5 (± 0·15)				
	18·0								0·55	0·6 [f]
Laminarin (insoluble)	285·0								0·0	0·0 [g]
Turanose	22·9					0·44		0·73		1·03
Maltulose monohydrate	22·1					0·0		0·0		0·0 [a]
Group C										
Sodium D-glucuronate monohydrate	62·1	0·58		0·93	0·98	0·93		1·07		1·06
D-Glucofuranurono-6→3-lactone	35·3				1·50	1·70 [i]		1·96		2·0
1 : 2-*iso*Propylidene-D-glucofuranurono-6→3-lactone	13·6					0·4	0·3			0·4 [j]
Sodium D-gluconate	22·3					0·0		0·0		0·0
D-Glucono-1→5-lactone	13·6					0·5	0·71			0·91
L-Gulono-1→4-lactone	15·1					0·66			0·61	0·62 [j]
	18·3					0·60		0·62		
D-Mannono-1→4-lactone	12·3					0·71				1·01 [k]
L-Galactono-1→4-lactone	16·5						1·07			
Lactobiono-1→5-lactone	12·4					0·0				0·0 [j]

[a] 1·03 at 45 min. [b] 0·95 at 45 min. [c] 1·06 at 2 hr. [d] At 12 hr. [e] At 10 hr. [f] At 12 hr. [g] At 20 hr. [h] At 9 hr. [i] 1·9 at 2 hr. [j] At 8 hr. [k] At 6 hr.

TABLE 2.

	$[\alpha]_D^{24}$ in borate: Concn. (%)	Time (min.) 1	2	3	4	5	10	15	30	$[\alpha]_D^{24}$ in water: $[\alpha]_D$			Concn. (%)
β-L-Arabinose	5·97	+139°	129°	120°	113°	108°	96°	90°	88·7°	191°	→	91·9°	6·02
α-D-Xylose	4·91	+38·9	30·8	25·0	21·6	20·1	18·5	18·5	18·5	93·6	→	17·0	5·11
D-Ribose	4·51	—	+8·4	10·0	—	9·1	—	8·5	8·5	−18·4	→	−19·8	5·15
α-D-Glucose	5·16	+54·0	51·2	48·6	47·7	46·6	46·3	46·1	45·9	112	→	49·1	5·03
β-D-Mannose	5·79	+ 5·7	9·0	9·9	9·9	9·9	10·0	9·9	—	−17·0	→	13·7	5·10
α-D-Galactose	2·35	+67·7	61·7	56·7	56·2	55·8	55·3	—	55·3	151	→	76·0	2·35

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Reduction of 2-Acetamido-2-deoxy-α-D-glucose.—A mixture of 2-acetamido-2-deoxy-D-glucose (0·55 g.) in 0·1M-boric acid solution (50 ml.) and 0·13M-potassium borohydride in 0·1N-sodium hydroxide solution (50 ml.) was kept for 2½ hr. at room temperature. Excess of borohydride was destroyed by a slight excess of glacial acetic acid, and the resulting solution concentrated to a dry white solid under reduced pressure. The solid was dissolved in a mixture of

TABLE 3.

pH *at* 19°

Concn.*	Ribose	Arabinose	Lyxose	Xylose	Concn.*	Ribose	Arabinose	Lyxose	Xylose
0·5	8·71	9·19	9·08	9·07	3	7·46	8·57	8·40	8·43
1	8·39	—	8·87	8·87	4	7·19	—	8·25	8·28
2	7·95	8·78	8·60	8·62	5	7·01	8·27	8·10	8·16

* Moles of pentose per mole of boric acid.

TABLE 4.

Pentose	Concn.*	pH at 17°	$K = [C^-]/[B^-][P]$	$K = [C^-]/[B^-][P]^x$	x
Ribose	8	6·63	$5{\cdot}21 \times 10^3$	$4{\cdot}39 \times 10^4$	1·84
	12	6·23	$8{\cdot}52 \times 10^3$	$5{\cdot}13 \times 10^4$	
	16	5·98	$1{\cdot}13 \times 10^4$	$5{\cdot}29 \times 10^4$	
	20	5·82	$1{\cdot}29 \times 10^4$	$5{\cdot}01 \times 10^4$	
Arabinose	8	8·09	$1{\cdot}67 \times 10^2$	$1{\cdot}73 \times 10^3$	1·90
	12	7·75	$2{\cdot}48 \times 10^2$	$1{\cdot}77 \times 10^3$	
	16	7·51	$3{\cdot}25 \times 10^2$	$1{\cdot}75 \times 10^3$	
	20	7·35	$3{\cdot}77 \times 10^2$	$1{\cdot}65 \times 10^3$	
Xylose	8	7·89	$2{\cdot}72 \times 10^2$	$2{\cdot}35 \times 10^3$	1·84
	12	7·35	$6{\cdot}4 \times 10^2$	$3{\cdot}96 \times 10^3$	
	16	7·08	$8{\cdot}87 \times 10^2$	$4{\cdot}24 \times 10^3$	
	20	6·86	$1{\cdot}18 \times 10^3$	$4{\cdot}68 \times 10^3$	

* Moles of pentose per mole of boric acid.

formamide (15 ml.) and dry pyridine (15 ml.), and redistilled acetic anhydride (15 ml.) was added. After 16 hr. the mixture was poured into ice-water (200 ml.), and the aqueous solution extracted with chloroform (2 × 200 ml.). The chloroform extract was shaken successively with 3N-hydrochloric acid (200 ml.), saturated aqueous sodium hydrogen carbonate (200 ml.), and water (400 ml.), and finally dried (Na_2SO_4). Concentration of the chloroform extract gave a syrup (0·31 g.) which on de-*O*-acetylation with ammonia (*d* 0·88; 6 ml.) in methanol (15 ml.) gave a crystalline product. After recrystallisation from ethanol, 2-acetamido-2-deoxy-D-glucitol was obtained as fine needles, m. p. 160°, $[\alpha]_D^{24}$ −9° (*c* 1·71 in water) (Found: C, 43·3; H, 7·8; N, 5·7. Calc. for $C_8H_{17}O_6N$: C, 43·1; H, 7·6; N, 6·3%). Karrer and Meyer [28] record m. p. 153°, $[\alpha]_D$ −11°.

We thank Dr. G. O. Aspinall, Dr. H. G. Fletcher, jun., and Professor J. K. N. Jones, F.R.S., for specimens, and the Medical Research Council for an award to one of us (P. D. B.).

THE UNIVERSITY, BRISTOL. [*Received, June 17th,* 1957.]

[27] Zill, Khym, and Cheniae, *J. Amer. Chem. Soc.*, 1953, **75**, 1339.
[28] Karrer and Meyer, *Helv. Chim. Acta*, 1937, **20**, 407.

871. *Intramolecular Non-bonded Effects involving Hydrogen Atoms.*

By K. E. Howlett.

Use of Hirshfelder and Linnett's potential function for the repulsive state of the hydrogen molecule is described for the purpose of calculating non-bonded energies between hydrogen atoms. When a suitable and intuitively reasonable dependence of this potential on the angle between the bonded and non-bonded direction is introduced, a quantitatively correct answer is computed for the rotational energy barrier in ethane. The same function is then applied to problems related to the diphenyl and *cyclo*hexane skeletons. The results are shown to be in general agreement with the known facts.

A major difficulty in any quantitative treatment of conformational analysis has proved to be the assignment of a suitable interaction potential function for two hydrogen atoms. Consideration of the apparently simple case of ethane, for example, has led to the unsatisfactory conclusion that, whereas it is not possible to account quantitatively for the potential barrier hindering free rotation in terms of van der Waals forces,[1] yet quadrupole interactions (assuming rather high quadrupole moments [2] or ionicities [3]) give answers of the correct order of magnitude. In other contexts the loose term van der Waals force is usually understood to include multipole interactions. However, by using the principle of the L.C.A.O. approximation, *viz.*, that in the regions of the hydrogen atoms the electron density is similar to that around an isolated hydrogen atom, the unnecessary and artificial assignment of a definite van der Waals radius may be avoided. Hirshfelder and Linnett [4] have given a thorough treatment of the potential of two hydrogen atoms. The mutual potential of two bound hydrogen atoms may be identified with Hirshfelder and Linnett's calculated potential for the repulsive state of the hydrogen molecule because, in each case, the Pauli principle may be invoked to show that the electrons on the two hydrogen atoms cannot occupy the same space. For the repulsive state of H_2 the electron-spin quantum numbers are the same, and for the hydrogen atoms considered in this paper, which are already linked to other atoms, the first quantum level is fully occupied so that the electrons on any other approaching hydrogen atom cannot also enter this level in the same spatial elements. Hirshfelder and Linnett's calculated curve is clearly of the correct form, passing from repulsion to slight attraction at large distances. The reality of the interaction may be gauged from the quantitative agreement of the calculated function with that deduced by Amdur and Mason [5] from collision experiments with hydrogen and helium. Use of the Hirshfelder–Linnett function yields larger repulsive potentials at short internuclear distances than those of earlier calculations [1] which were based on assigned van der Waals radii. This feature is a desirable one.[6] Employment of the function implies an extension in the use of data obtained for a spherically symmetrical electron distribution to cases of cylindrically symmetrical distributions. At present, unfortunately, non-bonded interaction calculations necessarily involve relatively crude assumptions.

Pauling,[7] and more specifically Hughes, Ingold, *et al.*,[8,9] suggest that the non-bonded interaction between two otherwise bound atoms should be somewhat dependent on the largest positive direction cosine of the non-bonded atom relative to the directly bound

[1] Barton, *J.*, 1948, 340.
[2] Lassettre and Dean, *J. Chem. Phys.*, 1948, **16**, 151, 553; 1949, **17**, 317.
[3] Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 79.
[4] Hirshfelder and Linnett, *J. Chem. Phys.*, 1950, **18**, 130.
[5] Amdur and Mason, *ibid.*, 1956, **25**, 630.
[6] Cf. Westheimer, "Steric Effects in Organic Chemistry," Ed. Newman, John Wiley, New York, 1956, p. 540.
[7] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, 1939, p. 178.
[8] Dostrovsky, Hughes, and Ingold, *J.*, 1946, 173.
[9] de la Mare, Fowden, Hughes, Ingold, and Mackie, *J.*, 1955, 3200.

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atoms (cf. Fig. 1). The form of variation used has effectively been to displace the potential curve laterally to greater separations by an amount $\chi(1 + \cos 2\theta)$ Å per non-bonded atom if $\theta < \pi/2$. For the particular interactions considered [8,9] χ was assigned the value 0·4 to give agreement with experiment, although this could be an overestimate since from Pauling's illustration [7] it yields virtually zero non-bonded interaction between the chlorine atoms in carbon tetrachloride. From the comparative failure of the simple valency force field (S.V.F.F.) treatment of the vibrational fundamentals for this molecule it seems probable that appreciable non-bonded effects are present.

In the present paper calculations are reported which use the Hirshfelder–Linnett repulsive potential function for non-bonded H–H interactions, and the numerical constant χ, required to allow for angular dependence of the interaction, has been varied from 0 to 0·4. The interaction energy is then summed over every possible pair of non-bonded atoms. The first computations concern the rotational energy barrier in ethane.

For each value of χ taken, the staggered form of ethane is found to be the most stable conformation (in agreement with experiment [10]), and the eclipsed form the least stable.

FIG. 1. *The ν_2 normal mode in ethane.*

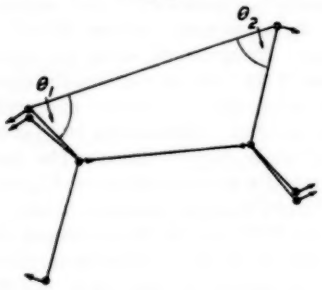
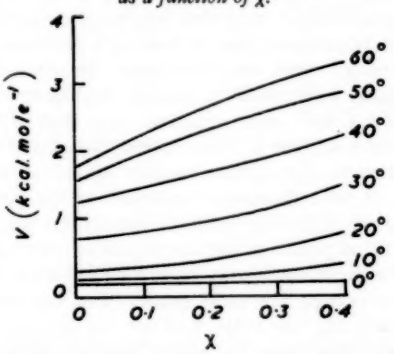


FIG. 2. *Variation of V with rotation in ethane as a function of χ.*



As in earlier calculations on this subject we have assumed that the molecule is rigid except in the rotation co-ordinate. Most of the vibration frequencies are sufficiently high to ensure that the vast majority of ethane molecules are in their ground vibrational states at ordinary temperatures. Therefore the most probable positions of the nuclei are the classical rigid positions. There are, however, appreciable uncertainties (zero-point amplitudes) about these positions. The normal vibrational mode which most affects the relative separation of the hydrogen atoms of the two methyl groups is the ν_2 mode (Fig. 1). Thus, although all the zero-point amplitudes ought to be considered, the ν_2 mode will probably affect the calculated barrier to the greatest extent. A crude assessment of this vibrational effect has been made by considering the motion as that of a 1-dimensional oscillator of frequency 1375 cm.$^{-1}$, with appropriate statistical weighting of configurations of various amplitudes. The vibrational effect in this mode is to raise the calculated barrier height by about 20% over that for the " rigid " model.

Contrary to opinions expressed earlier, the allowance for angular dependence of the effective van der Waals radius raises rather than lowers the barrier because, although it lowers most absolute potentials, it acts rather rapidly in a differential manner with angular rotation about the C–C bond. Most satisfactory, however, is the fact that the calculated barriers are all of the right order, and of the correct magnitude intermediately between the limits considered for the angular dependence function. Table 1 shows the dependence of the height of the barrier (V_0) (neglecting any vibrational effects) upon the assumed value of χ.

[10] Smith, *J. Chem. Phys.*, **1949**, **17**, 139.

Fig. 2 shows the variation of V with rotation (ϕ) about the C–C bond as a function of χ; ϕ is taken as 0 for the staggered conformation. The best value of χ is about 0·2. With this value, $V_0 = 2{\cdot}64$ kcal. mole^{-1} if the hydrogen atoms are always at the rigid positions,

TABLE 1.

χ	0	0·2	0·3	0·4
V_0 (kcal. mole^{-1})	1·77	2·64	2·91	3·25

and $V_0 \approx 3{\cdot}1$ kcal. mole^{-1} when the specified vibrational motion is considered. The angular variation of V (neglecting the vibrational effect) is compared in Fig. 3 with the frequently assumed function, $2V = V_0(1 - \cos 3\phi)$. The cosine barrier shape gives only moderate agreement with the present calculated curve. In fact, the calculated curve

FIG. 3. *Comparison of barrier shapes in ethane*: A, *calculated from non-bonded effects*; B, *cosine shape.*

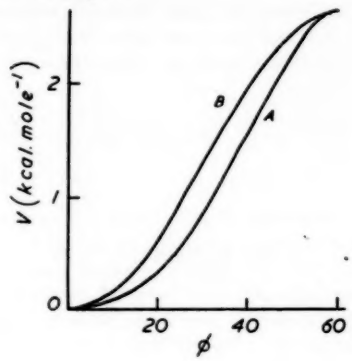
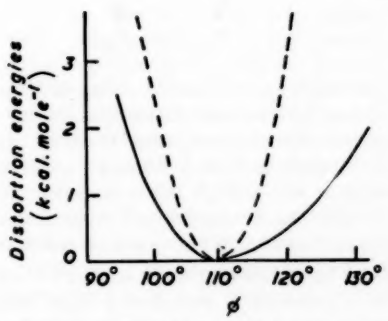


FIG. 4. *The ν_2 mode in methane.* (Broken curve shows one ψ contour for sp^3 orbital.)

FIG. 5. *Broken curve: total distortion energy. Full curve: non-bonded energy.*



corresponds more closely to case C mentioned by Pitzer and Gwinn.[11] Fortunately, as shown by Halford,[12] a difference of this kind from the cosine shape involves minute alterations in the calculated thermodynamic functions of the molecule.

The present result is frankly obtained to some extent by adjustment of the disposable parameter χ. A real test of the suitability of the potential function with $\chi = 0{\cdot}2$ lies in its applicability to other cases. Beginnings of such applications, together with the attendant difficulties, are discussed below.

(1) As a first illustrative use of the potential function we consider the ν_2 normal vibration in methane (Fig. 4). In the formation of the tetrahedrally spaced bonds, the molecular orbitals may be considered to be formed by overlap of hydrogen 1*s* atomic

[11] Pitzer and Gwinn, *J. Chem. Phys.*, 1942, **10**, 428.
[12] Halford, *ibid.*, 1947, **15**, 645.

orbitals with carbon sp^3 hybrid atomic orbitals. The density contours of the latter have relatively small curvature in the overlap region so that small vibrations in the ν_2 mode should not greatly affect the overlap. If we make the approximation that the hybridisation of the carbon atomic orbitals changes insignificantly during the vibration, then it is expected that the non-bonding effects should make an appreciable contribution to the rise in potential energy accompanying distortion in this mode. The total distortion energy is known in good approximation from the S.V.F.F. treatment for methane which yields the appropriate force constant of $0{\cdot}5 \times 10^{-11}$ erg radian^{-2} molecule^{-1}. The non-bonded contribution has been calculated by assuming that the C–H bond length is invariant at 1·094 Å throughout the vibration. A comparison of the two energies (summed in each case over the 6 possible interactions) is given in Fig. 5 as a function of one $\widehat{HCH}$ angle (ϕ). It appears that non-bonded effects are appreciable even in methane.

(2) Secondly, we consider the effect of non-bonded interaction on rotation about the 1 : 1′-bond in diphenyl (Fig. 6). The interplanar angle is denoted by ϕ. In order to proceed, the following assumptions are made. The variation of energy with ϕ is regarded as having three components: (*a*) the resonance energy, which has been taken from Guy;[13] (*b*) non-bonded interactions; and (*c*) in-plane bending effects (such as those through the

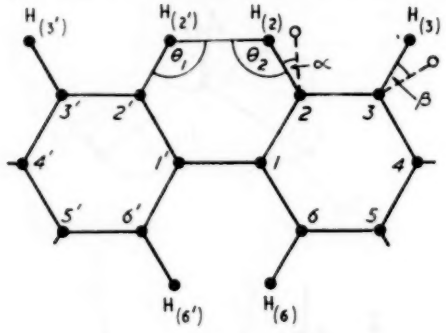


FIG. 6. *Diphenyl.*

four angles α in Fig. 6). Ring distortion has been neglected.[14] It has also been shown by a subsidiary calculation that energy recovery by bending the four angles β is negligible even in the coplanar conformation. The 1 : 1′-bond length is considered to vary with ϕ. It is taken as 1·54 Å when $\phi = \pi/2$, but shortened to a number of possibilities over the range 1·44—1·50 Å when $\phi = 0°$. In each case the relative shortening from 1·54 Å towards the assumed length when $\phi = 0°$ is taken as proportional to the resonance energy. The aromatic C–C bonds are all taken as 1·4 Å in length, the C–H bonds as 1·1 Å, and the $\widehat{CCH}$ bond bending force constant[15] as $0{\cdot}86 \times 10^{-11}$ erg radian^{-2} molecule^{-1}. Since this force constant is transferred from benzene, it may be assumed that distortion energies calculated with its aid already include non-bonding effects between, for example, H_2 and the $C_{(1')}$, $C_{(1)}$, $C_{(3)}$, and $H_{(3)}$ group. Non-bonding effects between (say) $H_{(2)}$ and $C_{(2')}$ have been neglected in the calculations. These effects are likely to be small. The uncertainty of position effect discussed for ethane has also been neglected.

For each conformation considered for the molecule, the energy is minimised by summing the effects (*a*), (*b*), and (*c*) over a number of configurations. Table 2 shows the calculated energy barrier (V_0) hindering free rotation of the rings as a function of the length, d(1 : 1′), of the central bond in the coplanar position. Also included in the table is the value of V_0 found if the central bond length is 1·54 Å independently of ϕ, and if there is no resonance energy contribution to the stability of the coplanar state. This figure supplies the

[13] Guy, *J. Chim. phys.*, 1949, **46**, 469.
[14] Cf. Westheimer, *J. Chem. Phys.*, 1947, **15**, 252.
[15] Kohlrausch, *Z. phys. Chem.*, 1935, **30**, *B*, 305.

justification for the inclusion of effect (*a*) in the total energy because delocalisation of the charge distribution can only contribute to the real structure of the coplanar (or any other) state if the lowering of potential energy due to resonance outweighs the rise in non-bonded energy consequent upon the bond shortening.

TABLE 2.

$d(1:1')$ (Å)	1·44	1·46	1·48	1·50	1·54
V_ϕ (kcal. mole^{-1})	11·5	10·8	10·1	9·5	(15·3)

Table 3 shows the variation in resonance energy,[13] bond shortening, $d(1:1')$, and the computed change in potential energy (V) as a function of ϕ, for the case in which $d(1:1')$ is 1·46 Å at $\phi = 0°$. As in the case of ethane, the shape of the barrier shows maxima only in the eclipsed positions, and it also shows the same type of variation from the cosine form (with two maxima and minima per revolution). A barrier of maximum height 10 kcal. mole^{-1} would give strong preference for conformations well away from coplanarity but would be insufficient to allow of separation of rotational isomers in suitably substituted

TABLE 3.

ϕ	0	$\frac{\pi}{16}$	$\frac{\pi}{8}$	$\frac{3\pi}{16}$	$\frac{\pi}{4}$	$\frac{5\pi}{16}$	$\frac{3\pi}{8}$	$\frac{7\pi}{16}$	$\frac{\pi}{2}$
Resonance energy (kcal. mole^{-1})	6·96	6·32	4·70	2·80	1·29	0·43	0·09	0	0
Central bond shortening (Å)	0·08	0·07	0·055	0·03	0·015	0·005	0	0	0
$d(1:1')$ (Å)	1·46	1·47	1·485	1·51	1·525	1·535	1·54	1·54	1·54
V (kcal. mole^{-1})	10·8	9·1	6·5	3·60	1·57	0·80	0·23	0·06	0

derivatives. Furthermore, the result may be correlated with experiment. Thus although the variation in resonance energy may be of the form suggested by Guy, the average resonance energy of diphenyl has been calculated[16] to be almost zero. The present calculations support the idea that most free diphenyl molecules will have interplanar angles greater than $\pi/4$. From this result, Guy's estimated average resonance energy would be 0—1 kcal. mole^{-1}. A necessary corollary to this conclusion is that the average central-bond-shortening in diphenyl is only about 0·01 Å. Also it is seen from Table 3 that the variation in V for a change in ϕ near $\phi = \pi/2$ is very small. Thus the restoring force constant for this mode is likewise small. (For the approximately quadratic increase in V as ϕ varies by up to $\pi/8$ from the potential minimum position, $k_\phi = 1 \times 10^{-13}$ erg radian^{-2} molecule^{-1}.) This implies that diphenyl will tend to populate not only the ground vibrational state but also the low-lying excited states in this interannular vibration mode. In fact, the maximum population density probably lies in one of the early excited levels. In such a level the most probable state of the molecule is near the limit of the classical amplitude where the vibrational wave function has its greatest values. Therefore, the instantaneous state of a free diphenyl molecule is most likely to be near that conformation at which the potential curve begins to rise more steeply, *i.e.*, in the region of $\phi \simeq 55°$. Bastiansen's electron-diffraction result[17] (which corresponds to a most probable instantaneous state) for ϕ is $45° \pm 10°$.

A final correlation with experiment is obtained by the following method. We make the approximation that 3 : 3'-dichlorodiphenyl has the same variation of intramolecular forces with ϕ as diphenyl itself, together with dipolar interactions arising from the 3- and 3'-substituents. The dipolar interaction energies have been computed by assuming two point dipoles of magnitude 1·58 D, situated at the "points of contact" of carbon and chlorine atoms, to be separated by a medium of dielectric constant 2·2. The addition of this electrostatic energy (which is positive for all conformations) to that computed for diphenyl itself yields a resultant potential curve with a minimum at about $\phi = 92°$, *i.e.*, with the chlorine atoms slightly *trans*. The dielectric-constant evidence[18] (obtained by using

[16] Klages, *Ber.*, 1949, **82**, 358.
[17] Bastiansen, *Acta Chem. Scand.*, 1949, **3**, 408.
[18] Littlejohn and Smith, *J.*, 1954, 2552.

radiofrequency and therefore giving an average figure for the dipole moment throughout the molecular vibrations) indicates that $\phi \simeq 97°$ with the chlorine atoms *trans*. The agreement is notable and shows that the relative magnitudes of the different effects are about correct.

(3) Some investigation has been made of non-bonding effects between hydrogen atoms in the *cyclo*hexane ring system. In conformity with earlier calculations,[1] the chair form of *cyclo*hexane is found to be more stable than the boat form. All angles are assumed to be tetrahedral. The more interesting isomer in the present calculations is the flexible one, because whilst the extreme boat form is calculated to be 8·0 kcal. mole^{-1} less stable than the chair form, the half-rotated form is only 4·0 kcal. mole^{-1} less stable.[19] Repulsive interactions with the carbon atoms have been neglected—clearly they would have little effect on the result.

In considering the limitations of the present method of computation it will be appreciated that it is impracticable to proceed to more complex molecules unless allowance is made for angular distortion. For example, in the absence of bond bending, *trans*-decalin is calculated to be 16 kcal. mole^{-1} more stable than the *cis*-linked double chair form; whilst the bending of only four C–H bonds by 5° in the *cis*-decalin would lower the overall energy discrepancy to about 11 kcal. mole^{-1}. Since the real strain would be spread over the whole molecule, further lowering would be effected, but, of course, it is impossible to recover the whole of the difference in stability by angular distortion.

Similarly, a direct comparison of equatorial and polar monomethyl*cyclo*hexane yields the correct qualitative result, *viz.*, that the equatorial form is the more stable, but the energy difference (18 kcal. mole^{-1}) calculated by using wholly tetrahedral angles is again too high.

It may be concluded that, although the method of computation is based upon a crude approximation, it yields reasonably quantitative results in simple molecules in which bond bending effects can be estimated with some precision.

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[19] Cf. Hazebroek and Oosterhoff, *Discuss. Faraday Soc.*, 1951, **10**, 87.

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872. *The Kinetics of Alkaline Hydrolysis of Ethyl Nitro-1-naphthoates.*

By A. FISCHER, J. D. MURDOCH, J. PACKER, R. D. TOPSOM, and J. VAUGHAN.

A study has been made of the kinetics of alkaline hydrolysis of the ethyl esters of 2-, 3-, 4-, 5-, 6-, and 8-mononitro- and of 4 : 5-dinitro-1-naphthoic acid, in ethanol–water, at four temperatures covering a range of 15°, 20°, or 30°. Results are compared with each other and with those obtained for benzoates, comments are made on Hammett σ values obtained in this and other work, and the steric effects connected with 2- and 8-nitro-substituents are discussed.

EXTENSIVE studies have been made of substituent effects on the reactivity of a side-chain in benzene derivatives.[1] Similar investigations on naphthalene derivatives have been few and, in pursuance of a general study of reactivity in the naphthalene series, we have examined the effect of the nitro-group on the rate of alkaline hydrolysis of ethyl 1-naphthoates in 85% ethanol–water (w/w). For the corresponding benzoate hydrolysis,

[1] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

substituent effects are well understood; the mechanism is known to involve acyl–oxygen fission [2] and to be of the first order with respect to both ester and base.[3]

Experimental

Esters.—Ethyl 2-[4] and 8-nitro-1-naphthoate [5] were prepared by the action of excess of ethyl iodide on the corresponding silver salts. They melted at 92° and 68° respectively. 2-Nitro-1-naphthoic acid (m. p. 202°) was made from 1-methylnaphthalene.[4] 8- and 5-Nitro-1-naphthoic acid were obtained by nitration of 1-naphthoic acid: [6] treatment of the mixture of acids with hydrogen chloride and ethanol converted the 5-nitro-acid into its ethyl ester (m. p. 94°); [7] the purified 8-nitro-acid melted at 220°. Ethyl 3- (m. p. 87°) and ethyl 4-Nitro-1-naphthoate (m. p. 57°) were obtained from the corresponding acids through the acid chlorides, the acids themselves (m. p.s 269° and 225·5° respectively) having been prepared from acenaphthene.[8] Ethyl 6-nitro-1-naphthoate (m. p. 111°) was prepared by treatment of the crude 6-nitro-acid (obtained by the evaporation of the mother-liquor from the recrystallization of the 3-nitro-acid) with hydrogen chloride and ethanol.[8] Ethyl 4 : 5-dinitronaphthoate was made by nitration of ethyl 5-nitro-1-naphthoate by Koelsch and Hoffmann's method.[7] Analytical figures were obtained for this ester in view of the polymorphism indicated by its behaviour on heating (Found: C, 54·0; H, 3·6; N, 9·75. Calc. for $C_{13}H_{10}O_6N_2$: C, 53·8; H, 3·5; N, 9·65%). The ester melted sharply at 140°. Then (i) further heating led to solidification followed by a sharp m. p. at 145·5°, and (ii) cooling and reheating the solidified sample resulted in a single m. p. of 145·5°.

Solvent.—Ethanol was purified by a preliminary distillation from sulphuric acid (45 ml. of 4N-acid per litre of alcohol),[9] followed by several treatments with silver oxide [10] and a final fractional distillation in hydrogen.[11] Only the middle fraction was used for kinetic runs. Boiled-out distilled water was used for making up solutions, and sodium hydroxide solutions were free from carbonate.

Apparatus.—Bath temperatures were maintained (thermostat) within ±0·02°. The conductivity bridge consisted of (i) a regulated power supply, (ii) a Wien bridge oscillator, producing a current of frequency *ca.* 1 kilocycle per sec., (iii) the Wheatstone bridge, which had 450 ohm fixed-ratio arms and a decade resistance box with a compensating variable condenser across it for the measuring arm, (iv) a high-gain amplifier, and (v) a detector unit. Balance was indicated by zero reading of the microammeter in the detector unit. For resistances of the order measured in runs (300—1200 ohms) the bridge had a maximum sensitivity better than 1 part in 100,000 and a stability, measured over a greater period of time than the maximum time for a kinetic run, of better than 1 part in 20,000. The conductivity cells used were of the type described by Evans and Hamann.[12] They consisted of a compartment of 15—20 ml. capacity, containing bright platinum electrodes, and a smaller compartment of 2—3 ml. capacity joined to the first by a hollow elbow. Each compartment had a filling tube.

Hydrolyses.—For the 2-, 3-, 4-, and 8-nitro-esters, kinetics were followed by conductivity methods. The following method was employed for the 3- and 4-nitro-esters (*i.e.*, for fast reactions).

The solution (9—10 g.) of the ester in 95% ethanol was weighed into the larger cell compartment. From the exact weight of ester solution taken, the required volume of aqueous sodium hydroxide solution to make the reaction mixture [85% ethanol–water (w/w) with ester and base in equimolar amounts] was measured into the smaller compartment. After the cell had come to temperature equilibrium with the bath, the contents were mixed and left in the

[2] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.
[3] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, 1953, Chapter XIV.
[4] Topsom and Vaughan, *J.*, 1957, 2842.
[5] Ekstrand, *J. prakt. Chem.*, 1888, **38**, 155.
[6] *Idem, ibid.*, p. 139.
[7] Koelsch and Hoffmann, *J. Amer. Chem. Soc.*, 1943, **65**, 989.
[8] Leuck, Perkins, and Whitmore, *ibid.*, 1929, **51**, 1831.
[9] Danner and Hildebrand, *ibid.*, 1922, **46**, 2824.
[10] Dunlap, *ibid.*, 1906, **28**, 395.
[11] Riiber, *Z. Elektrochem.*, 1923, **29**, 335.
[12] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 31.

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electrode compartment. After an initial 15 min. interval, 30 resistance–time measurements (*i.e.*, R_1, t_1; R_2, t_2; · · · · · R_{30}, t_{30}) were made at approximately equal increments of resistance. Zero time was the time of mixing.

From (i) the simplified form of the second-order rate equation

$$dx/dt = k(A_0 - x)^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ii) the relation between the resistance (R) of the solution and concentration (x) of carboxylate ion

$$x = a/R + b \text{ } (a \text{ and } b \text{ are constants}) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and (iii) the resistance–time values R_1/t_1, R_{11}/t_{11}, R_{21}/t_{21}, it follows that

$$A_0k = -\frac{\sum R_1R_{11}(t_{11} - t_1)}{\sum R_1R_{11}t_{21}(t_{11} - t_1)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where k is the rate constant, A_0 is the initial concentration of ester and base, and x (the concentration of carboxylate ion) is also the decrease in concentration of base or ester at time t (sec).

From expressions of type (3), ten values of A_0k were calculated for each run, and the mean was obtained.

The above method could not be satisfactorily applied to the very slow reactions of the 2- and 8-nitro-ester. A blank run, without added ester, indicated that the rate of increase of resistance (assumed to be caused by reaction of base and Pyrex cell-wall) was of the same order as that of rate of change in resistance observed in the hydrolysis of ethyl 8-nitro-1-naphthoate. This blank is insignificant with the 3- and the 4-nitro-ester (k values for these are *ca.* 5000 × k for the 8-nitro-ester). The following method was adopted for measuring hydrolysis of the two hindered esters. An 85% ethanol–water solution of sodium hydroxide was made up in the electrode compartment of a cell. After temperature equilibrium with the bath had been attained, eight measurements of the resistance were made during 1 hr. (blank run). The calculated quantity of ester was added and the cell resistance measured at frequent intervals covering 3 hr. after mixing.

From the limiting conditions (i) $x = 0$, $R = R_0$, and (ii) $x = A_0$, $R = R_\infty$, and equations (1) and (2),

$$R = \frac{R_0}{R_\infty} A_0k(R_\infty - R)t + R_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

When k is small, $(R_\infty - R)$ is approximately constant and thus R is a linear function of t. Plots of R against t were made for the blank and the hydrolysis runs. The "hydrolysis" plot was extrapolated back to the time of ester addition ($t = 0$) to find R_0. The difference in slopes of "hydrolysis" and "blank" plots gave the rate of change in resistance for ester hydrolysis alone, *i.e.*, $(R_\infty - R)A_0kR_0/R_\infty$. As a measure of R_∞ the resistance was measured of the corresponding solution of the sodium salt of the acid. Substitution of values for R_0, R_∞, R, and A_0 in the last expression gave k. It is to be noted that for faster reactions, when $(R_\infty - R)$ is no longer constant and the R–t plot no longer linear, it is possible to plot $(R - \alpha t)$ against $(R_\infty - R + \alpha t)t$ to give a linear plot with intercept R_0. Here α is the slope of the "blank" plot and $(R - \alpha t)$ is thus the resistance (at time t) caused by the hydrolysis alone. The slope of this plot is A_0kR_0/R_∞, and k is obtained by substituting values of R_0, A_0, and R_∞.

A titration method was used in following the hydrolysis of the 5- and 6-nitro- and 4 : 5-dinitro-ester. Solutions were made up as described for hydrolysis of the 3- and 4-nitro-ester and Evans, Gordon, and Watson's procedure [13] was followed in analysing reaction mixtures. Blank runs (without added ester) indicated no significant consumption of alkali. Runs were followed to 50% hydrolysis, good second-order kinetics being obtained. A few runs, using the titration method and with unequal concentrations of ester and base, were carried out on the 3-, 4-, and 5-nitro- and 4 : 5-dinitro-ester. The reaction was thereby shown to be of the first order with respect to both ester and base. Satisfactory agreement was found when the rate constants for the 3- and 4-nitro-esters were determined by both the conductivity and the titration method.

For each compound, kinetics were followed at a minimum of four temperatures. Use of the

[13] Evans, Gordon, and Watson, *J.*, 1937, 1430.

Arrhenius equation ($\log k = \log B - E/RT$) led to linear plots of $\log k$ against $1/T$ in every case except that of the 2-nitro-ester. With this ester a distinct curvature indicated that k was increasing more rapidly with T than would be indicated by the best straight-line fit to the points. Mean rate data and probable errors for all esters are listed in Table 1, together with derived values of Arrhenius parameters. The latter values have a probable error of 1%, except those for the 2-nitro- (5%) and 8-nitro- (2%) esters. Beneath each mean value of k, the number of runs is given in parentheses.

TABLE 1.

10^5k (l. mole^{-1} sec.$^{-1}$).

Ethyl x-*nitro*-1-*naphthoates.*

x	20°	30°	35°	40°	50°	55°	60°	65°
2	—	—	—	—	0·332 ±0·002 (2)	0·44 ±0·02 (2)	0·65 ±0·02 (4)	1·05 ±0·04 (2)
3	—	17·1 ±0·6 (5)	26·9 ±0·3 (5)	41·0 ±0·1 (3)	92·3 ±0·1 (2)	—	—	—
4	—	19·0 ±0·0 (2)	28·8 ±0·1 (3)	44·4 ±0·2 (5)	101±2	—	—	—
5	2·61 ±0·02 (3)	6·37 ±0·09 (6)	9·5 ±0·2 (3)	15·1 ±0·1 (4)	34·5 ±0·1 (4)	—	—	—
6	2·40 ±0·04 (3)	5·91 ±0·05 (3)	—	13·7 ±0·1 (3)	29·9 ±0·1 (3)	—	—	—
8	—	—	—	—	0·0256 ±0·0001 (3)	0·041 ±0·002 (2)	0·066 ±0·002 (3)	0·097 ±0·004 (2)

Ethyl 4 : 5-*dinitronaphthoate*

Temp.	10^5k
5°	38·0 + 0·5 (5)
10	62·4 ± 0·1 (3)
15	98 ± 2 (3)
20	158 ± 2 (4)

x	E (kcal. mole^{-1})	log B
2	16·6	7·7
3	16·4	10·0
4	16·3	10·0
5	16·2	9·5
6	15·8	9·2
8	19·7	8·7
4 : 5-Di	15·3	10·6

DISCUSSION

Evans, Gordon, and Watson[13] have shown that for the alkaline hydrolysis of unsubstituted and of *meta*- and *para*-substituted ethyl benzoates in 85% ethanol–water, log B is constant within experimental error. For hydrolysis of *ortho*-substituted ethyl benzoates log B is smaller and is not constant. For the alkaline hydrolysis of ethyl benzoate in 87·83% ethanol, log $k_{30} = -3{\cdot}08$, log $B = 7{\cdot}3$, and $E = 14{\cdot}4$ kcal. mole^{-1}.[14] In 85% ethanol, log $k_{30} = -2{\cdot}98$, log $B = 9{\cdot}8$, and $E = 17{\cdot}7$ kcal. mole^{-1}.[13] A small solvent change thus has an extremely large effect on the Arrhenius parameters (but not on log k_{30}). In the present work log B values for the 3- and the 4-nitro-compounds are slightly higher than might have been expected. For work on these two compounds a fresh solvent batch was used and although care was naturally exercised a slight variation in make-up of batches may have existed. It is therefore suggested that the alkaline hydrolyses of mononitronaphthoates here reported (with the exception of the 2- and 8-nitro-compounds) can also be regarded as iso-entropic, within the limits of experimental error. Values of $\Delta\Delta G^{\ddagger}$ ($= -RT \ln k/k_0$), $\Delta\Delta H^{\ddagger}$ ($= \Delta E$), $T\Delta\Delta S^{\ddagger}$ ($= -RT \ln B/B_0$), and Hammett substituent constant [$\sigma = (1/\rho) \log k/k_0$] for both benzoates and naphthoates are collected in Table 2. The values for nitro-1-naphthoates are relative to ethyl 1-naphthoate ($E = 17{\cdot}22$; log $B = 9{\cdot}01$).[15] The values for nitrobenzoates are relative to ethyl benzoate ($E = 17{\cdot}79$; log $B = 9{\cdot}83$).[13] Values of the Hammett reaction constant ρ, used to evaluate substituent constants, were taken from Jaffé's review. The figures for ethyl nitrobenzoates are

[14] Herbst and Jacox, *J. Amer. Chem. Soc.*, 1952, **74**, 3004.
[15] Personal communication from J. E. Packer.

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calculated from the *rate constants* of Evans, Gordon, and Watson,[13] who appear to have made an error in calculating E and log B for the *o*-nitrobenzoate.

The values, in parentheses, for $\Delta\Delta H^{\ddagger}$ have been derived from values of $\Delta\Delta G^{\ddagger}$, on the assumption that $\Delta\Delta S^{\ddagger} = 0$. Over small temperature ranges, experimental errors in E and log B tend to be self-cancelling in their effect on k. Hence, in these cases $\Delta\Delta G^{\ddagger}$ is more reliable than ΔE as a measure of $\Delta\Delta H^{\ddagger}$.

TABLE 2.

x	Temp. (° K)	$\Delta\Delta G^{\ddagger}$ (kcal. mole^{-1})	$\Delta\Delta H^{\ddagger}$ (kcal. mole^{-1})	$T\Delta\Delta S^{\ddagger}$ (kcal. mole^{-1})	σ
		Ethyl x-*nitro*-1-*naphthoates*			
2	323·2	+1·3	−0·6	−2·0	—
3	323·2	−2·4	(−2·4)	—	0·68
4	323·2	−2·4	(−2·4)	—	0·70
5	323·2	−1·7	(−1·7)	—	0·50
6	323·2	−1·7	(−1·7)	—	0·48
8	323·2	+3·0	+2·5	−0·5	—
4 : 5-di	298·2	−4·1	(−4·1)	—	1·18
		Ethyl x-*nitrobenzoates*			
2	323·2	−1·2	−2·6	−1·4	—
3	308·2	−2·5	(−2·5)	—	0·73
4	308·2	−2·8	(−2·8)	—	0·81

Examination of tabulated σ values reveals three interesting features. (i) The nitro-substituent exerts a slightly smaller polar effect in the naphthoates than it does in the corresponding position in benzoates. (ii) However, for the 3-position, and for the 4-position, in benzoates and naphthoates, the polar effects are sufficiently similar to justify the assumption that the same general mechanism applies to both series. (iii) Polar effects of the 3- and 4-nitro-substituents are much closer in magnitude in the naphthoates than in the benzoates. Concerning (iii), if the nitro-group is to exert its full $-T$ effect it must lie approximately in the plane of the ring. Stuart models indicate that in the 4-position of naphthalene it is prevented from doing so by the adjacent *peri*-hydrogen atom. It follows that the $-T$ effect is reduced and the σ value is also reduced, in the direction of σ for the 3-nitro-substituent. Comparison of σ values for the 5- and the 6-nitro-substituent apparently reveals a similar effect. The 5-nitro-substituent, which is conjugated with the 1-position, has only a little greater polar effect than the 6-nitro-, which is not conjugated with the 1-position. However, an additional factor can be considered in this case. Examination of possible resonance structures indicates that the contribution of the $-T$ effect to the total σ value for the 5-nitro-substituent should be less than that of the $-T$ effect for a 4-nitro-substituent in 1-naphthyl compounds.

It is noteworthy that σ for the " dinitro "-substituent is approximately equal to the sum of the σ values for 4- and 5-mononitro-substituents. This apparent additivity might be taken to imply that any further deviation from coplanarity (resulting from substitution of *peri*-H by NO_2) has little effect on these σ values.

Table 3 summarises all available σ values for nitro-substituents in 1-naphthyl derivatives. Values in columns 2 and 3 are those given by Price *et al.*[16] Figures in column 4 are calculated from Schreiber and Kennedy's results, [17] and values in the last column are similarly calculated from Bryson's data.[18] The symbol in parentheses, σ−, conforms with the symbolism recently agreed on by Brown, Deno, Jaffé, Taft, and others.[19] It is equivalent to the symbol σ* adopted earlier by Hammett.

Values for σ in the last column are lower than those elsewhere in the Table, but otherwise agreement is as good as that found for benzene derivatives. It is to be noted that

[16] Price, Mertz, and Wilson, *J. Amer. Chem. Soc.*, 1954, **76**, 5131.
[17] Schreiber and Kennedy, *ibid.*, 1956, **78**, 153.
[18] Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257; 1951, **47**, 528.
[19] Taft, personal communication, and *J. Amer. Chem. Soc.*, 1957, **79**, 1045.

the work on naphthols and on naphthylammonium ions does not indicate the necessity for a σ– value in the case of the 5-nitro-substituent. Thus with 1-naphthyl derivatives, the $-T$ effect of a 5-nitro-substituent appears to be much less important than that of a 4-nitro-group, as tentatively suggested earlier in this discussion

TABLE 3.

	Ester hydrolysis (85% EtOH)	Ester hydrolysis (70% dioxan)	pK_a (naphthoic acids)	pK_a (naphthols)	pK_a (naphthyl-ammonium ions)
3-Nitro	0·68	—	—	—	0·61
4-Nitro	0·70	0·67	0·64	1·71 (σ–)	1·23 (σ–)
5-Nitro	0·50	0·49	0·43	0·57	0·40
6-Nitro	0·48	—	—	0·43	0·30
7-Nitro	—	—	—	—	0·70
4 : 5-Dinitro	1·18	—	—	—	—

Steric effects are of importance in the hydrolysis of the 2- and 8-nitro-1-naphthoate and the available data allow a rough comparison of the steric contributions in the two cases. Two types of primary steric effect must be distinguished:[20] (i) steric strain, arising from overlap between non-bonded atoms, and (ii) steric interference with motions. Other things being equal, an increase in steric strain in going from reactant to transition state will result in an increase in the heat of activation, whereas an increase in the " steric interference with motions " factor will lead to a decrease in the entropy of activation. Both will cause an increase in the free energy of activation. For the 2-nitro-1-ester, a rough estimate may be made of steric effects, on the assumption that the polar contribution to the relative heat of activation is not substantially different from that in the case of *o*-nitrobenzoate (−2·6 kcal. mole^{-1} from Table 2). This, of course, also carries the further assumption that there is little change in steric strain, for *o*-nitrobenzoate, in passing from reactant to transition state. Models, and the comparable $\Delta\Delta H^{\ddagger}$ values for ethyl nitrobenzoates (Table 2), support this. Thus the steric contribution to $\Delta\Delta H^{\ddagger}$ is *ca.* +2 kcal. mole^{-1} (*i.e.*, $\Delta\Delta H^{\ddagger} + 2{\cdot}6$). From Table 2 the steric hindrance contribution to the total steric effect is +2 kcal. mole^{-1}, *i.e.*, the two steric contributions are comparable in magnitude.

Steric effects for the 8-nitro-substituent may be estimated by assuming that the polar contribution is somewhat similar to that of a 6-nitro-substituent (−1·7 kcal. mole^{-1}). The steric strain contribution to $\Delta\Delta H^{\ddagger}$ is *ca.* 4·2 kcal. mole^{-1} (*i.e.*, $\Delta\Delta H^{\ddagger} + 1{\cdot}7$). In this case, unlike that of the 2-nitro-ester, the steric hindrance contribution (0·5 kcal. mole^{-1} from Table 2) to the total steric effect is almost negligible compared with the contribution of the steric strain term. Examination of models, in fact, suggests that in going from the 2-nitro-ester to the transition state there is little increase in strain whereas in the case of the 8-nitro-ester the corresponding increase is great.

Two further comments may be made on the 2-nitro-ester hydrolysis. First, the fact that $\Delta\Delta G^{\ddagger}$ is large and positive, whereas $\Delta\Delta G^{\ddagger}$ for *o*-nitrobenzoate is large and negative, appears to illustrate the so-called " buttress " effect. Presumably, in *o*-nitrobenzoate some of the steric interaction is relieved by deformation of bond angles. In the 2-nitronaphthoate the ethoxycarbonyl group cannot bend away from the 2-nitro-substituent without more serious interference with the *peri*-hydrogen atom. Secondly, the discernible curvature of the Arrhenius plot for the 2-nitronaphthoic ester is consistent with reaction by two mechanisms over the temperature range covered. With increase in temperature it might be expected that the reaction mechanism will change from predominantly acyl–oxygen fission to alkyl–oxygen fission. It is intended to carry out further work on the hydrolysis of 2- and of 8-substituted 1-naphthoic esters.

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[20] Taft, personal communication, and *J. Amer. Chem. Soc.*, 1953, **75**, 4534.

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873. *Steroids and Walden Inversion. Part XXXVIII.* The Deamination of Epimeric Cholestan-2-, -4-, and -7-ylamines.*

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Deamination in aqueous acetic acid of the equatorial cholestan-2α-, -4α-, and -7β-ylamines gives cholestan-2α-, -4α-, and -7β-ol respectively in high yield unaccompanied by the epimeric alcohols. The axial cholestan-2β-, -4β-, and -7α-ylamines yield cholestan-2β-, -4β-, and -7α-ol respectively accompanied by much cholest-2-, -4-, and -7-ene, respectively.

Shoppee, Evans, and Summers [1] found that deamination in aqueous acetic acid of epimeric 3- and 6-amino-steroids follows a strict stereochemical pattern; the equatorial amines react with retention of configuration to afford the appropriate equatorial alcohols in quantitative yield, whilst the axial amines react, also with retention of configuration, uniquely to furnish the appropriate axial alcohols accompanied by much elimination, the olefins produced conforming to the Saytzeff rule. A preliminary examination of the deamination of the epimeric cholestan-7-ylamines was reported; this work has now been completed and the investigation extended to include the epimeric cholestan-2- and -4-ylamines.

The epimeric bases were prepared by the standard methods; the oximes of cholestan-2-,[2] -4-,[3] and -7-one [4] on reduction with sodium–ethanol gave cholestan-2α-, -4α-, and -7β-ylamine (NH_2 : equatorial), and on catalytic reduction with platinum–acetic acid gave the epimeric cholestan-2β-, -4β-, and -7α-ylamines (NH_2 : axial).

Eckhardt [5] had previously prepared the *N*-acetyl derivatives of 3β-hydroxycholest-5-en-7α- and -7β-ylamine, obtained by sodium–ethanol reduction of 3β-acetoxycholest-5-en-7-one oxime. In a repetition of this work Barnett, Ryman, and Smith [6] succeeded in separating the free bases by fractional crystallisation; they also describe 3β-hydroxycholestan-7α-ylamine, m. p. 87—89°, $[\alpha]_D$ −143°, but it is evident from the rotation that the hydrogenation of 3β-hydroxycholest-5-en-7α-ylamine was incomplete.

The configurations assigned here are based on analogy, unsupported by independent proof as in the previous work,[1] but we regard them as tolerably secure.

The molecular-rotation contributions of the 2-, 4-, and 7-hydroxyl and -acetoxyl groups are set out in Table 1. It will be seen that the values form a consistent series with the β-epimeride always the more dextrorotatory.

In Table 2 are given the molecular-rotation contributions of the 2-, 4-, and 7-amino- and -acetamido-groups. It is seen that the values (except for 4β-acetamidocholestane) again form a consistent series, parallel to that shown in Table 1, and with the β-epimeride always the more dextrorotatory. These comparisons strongly support, if they do not prove, our assignments of configuration to the various pairs of epimeric bases.

The results of the deaminations are set out in Table 3, and reproduce the stereochemical pattern found previously [1] and described above.

The epimeric cholestan-7-ylamines possess purely equatorial and purely axial character respectively, because ring B has a rigid chair conformation on account of double locking by rings A and C. The formation of a single cholestan-7-ol with retention of configuration from each base indicates that partial axial character, arising from chair–boat interconversions, is not a factor in the stereochemical course of deamination of 2-, 3-, and 4-amino-steroids.

* Part XXXVII, *J.*, 1957, 3100.

[1] Shoppee, Evans, and Summers, *J.*, 1957, 97.
[2] Ruzicka, Plattner, and Furrer, *Helv. Chim. Acta*, 1944, **27**, 524.
[3] Barton and Rosenfelder, *J.*, 1951, 1048.
[4] Cremlyn and Shoppee, *J.*, 1954, 3515.
[5] Eckhardt, *Ber.*, 1938, **71**, 461.
[6] Barnett, Ryman, and Smith, *J.*, 1946, 528.

TABLE 1.

	$[M]_D$ ROH	$[M]_D$ parent compound	ΔM_D	$[M]_D$ ROAc	$[M]_D$ parent compound	ΔM_D
Cholestan-2α-ol	+101°	+ 91°	+ 10°	+ 61°	+ 91°	− 30°
Cholestan-2β-ol	+132	+ 91	+ 41	+114	+ 91	+ 23
Cholestan-4α-ol	+ 19	+ 91	− 72	+ 7	+ 91	− 84
Cholestan-4β-ol	+116	+ 91	+ 25	+ 84	+ 91	− 7
Cholestan-7α-ol	+ 43	+ 91	− 48	− 52	+ 91	−143
Cholestan-7β-ol	+202	+ 91	+111	+262	+ 91	+171
Cholestane-3β : 7α-diol	+ 32	+ 93	− 61	− 79 *	+ 60	−139
Cholestane-3β : 7β-diol	+214	+ 93	+121	+268 *	+ 60	+208
Cholest-5-ene-3β : 7α-diol	−382	−151	−231	−850 *	−205	−645
Cholest-5-ene-3β : 7β-diol	+ 29	−151	+180	+262 *	−205	+467

* 3 : 7-Diacetate.

TABLE 2.

	$[M]_D$ NH_2	$[M]_D$ parent compound	ΔM_D	$[M]_D$ NHAc	$[M]_D$ parent compound	ΔM_D
Cholestan-2α-ylamine	+ 77°	+ 91°	− 14°	− 61°	+ 91°	−152°
Cholestan-2β-ylamine	+110	+ 91	+ 19	+118	+ 91	+ 27
Cholestan-4α-ylamine	+ 41	+ 91	− 50	+155	+ 91	+ 64
Cholestan-4β-ylamine	+233	+ 91	+142	+142	+ 91	+ 51
Cholestan-7α-ylamine	− 77	+ 91	−169	+ 17	+ 91	+ 81
Cholestan-7β-ylamine	+209	+ 91	+118	+262	+ 91	+171
3β-Hydroxycholestan-7α-ylamine	− 97	+ 93	−190	− 40	+ 93	−133
3β-Hydroxycholestan-7β-ylamine	+411	+ 93	+318	+280	+ 93	+187
3β-Hydroxycholest-5-en-7α-ylamine	−1395	−151	−1244	−797	−151	−646
3β-Hydroxycholest-5-en-7β-ylamine	+822	−151	+973	+359	−151	+510

TABLE 3.

Amine	Conformn. of NH_2	Product of substitution	Product of elimination
Cholestan-2α-yl	e	Cholestan-2α-ol (96%) Cholestan-2β-ol (0%)	—
Cholestan-2β-yl	a	Cholestan-2β-ol (21%) Cholestan-2α-ol (0%)	Cholest-1- and -2-ene (74·5%)
Cholestan-4α-yl	e	Cholestan-4α-ol (82%) Cholestan-4β-ol (0%)	—
Cholestan-4β-yl	a	Cholestan-4β-ol (0%) Cholestan-4α-ol (0%)	Cholest-4-ene (92%)
Cholestan-7α-yl	a	Cholestan-7α-ol (36·5%) Cholestan-7β-ol (0%)	Cholest-7-ene (61%)
Cholestan-7β-yl	e	Cholestan-7β-ol (95%) Cholestan-7α-ol (0%)	—
3β-Hydroxycholest-5-en-7α-yl	a	Cholest-5-ene-3β : 7α-diol (22%) Cholest-5-ene-3β : 7β-diol (0%)	Cholesta-5 : 7-dien-3β-ol (70%)
3β-Hydroxycholest-5-en-7β-yl	e	Cholest-5-ene-3β : 7β-diol (84%) Cholest-5-ene-3β : 7α-diol (0%)	—
3β-Hydroxycholestan-7α-yl	a	Cholestane-3β : 7α-diol (23%) Cholestane-3β : 7β-diol (0%)	Cholest-7-en-3β-ol (59%)
3β-Hydroxycholestan-7β-yl	e	Cholestane-3β : 7β-diol (75%) Cholestane-3β : 7α-diol (0%)	—
Cholest-4-en-7β-yl	e	Cholest-4-en-7β-ol (86·5%) Cholest-4-en-7α-ol (0%)	—

Product alcohols isolated as acetates, but yields are for pure alcohols calculated from the yields of acetates.

In the case of axial cholestanylamines, there appears to be a connexion between the degree of steric hindrance to the approach of the entity which furnishes the hydroxyl group eventually found in the appropriate axial cholestanol and product composition.

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The order of decreasing steric hindrance at the relevant nuclear carbon atoms, estimated by consideration of the number and character of the 1 : 3-interactions, is: $4\beta = 6\beta > 2\beta > [1\alpha] = >7\alpha > 3\alpha$. This sequence is also that of decreasing production of olefin (92, 99, 75, 61, 54%) and of increasing production of axial alcohol (0, 0, 21, 37, 45%).

It should be noted that the olefin produced by deamination of cholestan-4β-ylamine is cholest-4-ene unaccompanied by cholest-3-ene, and that cholestan-7α-ylamine gives cholest-7-ene, unaccompanied by cholest-6-ene; these eliminations thus conform to the Saytzeff rule and not to the Hofmann rule.

Experimental

For general experimental directions, see Shoppee, Evans, and Summers.[1] $[\alpha]_D$ are in $CHCl_3$.

Deamination of Steroid Amines.—In the following eleven experiments the steroid amine was dissolved in either glacial acetic acid or 50% acetic acid and where necessary dioxan was added to cause complete dissolution. Sodium nitrite (approximately two to three times the weight of amine) in either water or 50% acetic acid was added, and the mixture left overnight at 20°. After neutralisation with 4N-sodium hydroxide the product was isolated by extraction with ether and then hydrolysed for 0·5 hr. with 5% methanolic potassium hydroxide or acetylated with acetic anhydride at 100°. Chromatographic separations were carried out on activated aluminium oxide (Spence, Type " H," 30 × wt. of product).

(1) Cholestan-2α-ylamine (292 mg.) gave a product which by chromatography yielded a solid (280 mg.; eluted with ether) which by recrystallisation from acetone gave cholestan-2α-ol, m. p. 178—80°, $[\alpha]_D$ +25·7° (*c* 0·88). Acetylation with boiling acetic anhydride gave an oil which by crystallisation from acetone–methanol gave *2α-acetoxycholestane*, m. p. 60—62°, $[\alpha]_D$ +14° (*c* 1·4) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 81·0; H, 11·9. $C_{29}H_{50}O_2$ requires C, 80·9; H, 11·7%].

(2) Cholestan-2β-ylamine as its *iso*propylidene derivative (210 mg.) gave a product which by chromatography yielded an oil (135 mg.; eluted with pentane) which by recrystallisation from acetone gave a mixture of cholest-1- and -2-ene, m. p. 68—71°, $[\alpha]_D$ +47° (*c* 0·98). Elution with ether gave a solid (41 mg.) which by recrystallisation from acetone–pentane gave cholestan-2β-ol, m. p. 155°, $[\alpha]_D$ +33° (*c* 1·0).

(3) Cholestan-4α-ylamine (17 mg.) gave a solid (14 mg.; eluted with benzene) which by crystallisation from methanol yielded cholestan-4α-ol, m. p. 189—190°.

(4) Cholestan-4β-ylamine (80 mg.) gave an oil (71 mg.; eluted with pentane) which by crystallisation from acetone furnished cholest-4-ene, m. p. 79—80°, $[\alpha]_D$ +73° (*c* 1·2).

(5) Cholestan-7α-ylamine (300 mg.) gave an oil (174 mg.; eluted with pentane) which by recrystallisation from acetone yielded cholest-7-ene, m. p. 75—78°, $[\alpha]_D$ +10° (*c* 1·4). Elution with benzene–pentane (1 : 1) and benzene furnished an oil (110 mg.) which by crystallisation from methanol gave cholestan-7α-ol, m. p. 94—96°.

(6) Cholestan-7β-ylamine (200 mg.) gave a solid (180 mg.; eluted with benzene) which by crystallisation from methanol gave cholestan-7β-ol, m. p. 112—113°.

(7) 3β-Hydroxycholest-5-en-7α-ylamine (100 mg.) gave a solid (75 mg.; eluted with 1 : 4 benzene–pentane) which by crystallisation from acetone furnished 7-dehydrocholesteryl acetate, m. p. 127—129°, $[\alpha]$ −83° (*c* 2·2). Elution with benzene afforded cholest-5-ene-3β : 7α-diol diacetate, m. p. 123° (25 mg.), after crystallisation from aqueous acetone.

(8) 3β-Hydroxycholest-5-en-7β-ylamine (210 mg.) gave an oil (213 mg.; eluted with benzene) which by crystallisation from ether–methanol yielded cholest-5-ene-3β : 7β-diol diacetate, m. p. 107—109°, $[\alpha]_D$ +53° (*c* 1·01).

(9) 3β-Hydroxycholestan-7α-ylamine (150 mg.) gave a solid (95 mg.; eluted by 2 : 3 benzene–pentane) which by crystallisation from acetone gave cholest-7-en-3β-yl acetate, m. p. 116—118°, $[\alpha]_D$ +0° (*c* 1·2), probably contaminated with a trace of cholest-6-en-3β-yl acetate, m. p. 112—113°, $[\alpha]_D$ −89°. Successive elution with benzene–pentane (1 : 1) and benzene yielded a solid (43 mg.) which by crystallisation from methanol gave cholestane-3β : 7α-diol diacetate, m. p. 136—138°.

(10) 3β-Hydroxycholestan-7β-ylamine (200 mg.) gave a solid (182 mg.; eluted by 1 : 1 benzene–pentane) which by crystallisation from methanol gave cholestane-3β : 7β-diol diacetate, m. p. 84—86°, $[\alpha]_D$ +54° (*c* 0·8).

(11) Cholest-4-en-7β-ylamine (400 mg.) gave an oil (350 mg.; eluted by pentane) which by crystallisation from acetone gave cholest-4-en-7β-yl acetate, m. p. 95—98° $[\alpha]_D$ +72° (*c* 1·1). Elution with benzene gave 7β-acetamidocholest-4-ene, m. p. 196—198° (41 mg.).

Cholestan-2α-ylamine.—Cholestan-2-one oxime {m. p. 200—202°, $[\alpha]_D$ +7° (*c* 1·0); 900 mg.} in refluxing propan-2-ol (50 c.c.) was treated with sodium until a saturated solution was formed. The solution was worked up in the usual manner, to give an oil (840 mg.) which was chromatographed on aluminium oxide (30 g.). Successive elution with ether–benzene (1 : 1), ether, ether–methanol (9 : 1), and methanol gave oils (725 mg.) which by crystallisation from pentane yielded *cholestan-2α-ylamine* as rods, m. p. 111—113°, $[\alpha]_D$ +20° (*c* 0·97) [Found (after drying at 20°/0·03 mm. for 6 hr.): C, 83·4; H, 12·5. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. Acetylation with acetic anhydride in ether at 15° gave a solid which by recrystallisation from ethyl acetate afforded *2α-acetamidocholestane* as needles, m. p. 215—216°, $[\alpha]_D$ −14° (*c* 1·0) [Found (after drying at 50°/0·03 mm. for 3 hr.): C, 81·2; H, 11·8. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-2β-ylamine.—Cholestan-2-one oxime (906 mg.) in glacial acetic acid (30 c.c.) was shaken in hydrogen with platinum oxide (281 mg.); the theoretical uptake of hydrogen was attained in 3 hr. The product after basification with ammonia was chromatographed on aluminium oxide (30 g.). Successive elution with ether–benzene (1 : 1), ether, ether–methanol (9 : 1), and methanol gave oils (789 mg.) which solidified, to give cholestan-2β-ylamine, m. p. 70—76°, $[\alpha]_D$ +28·4° (*c* 1·2). Crystallisation from acetone gave 2β-iso*propylideneamino*-*cholestane* as rods, m. p. 115—117°, $[\alpha]_D$ +4° (*c* 1·1) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 83·9; H, 12·5. $C_{30}H_{53}N$ requires C, 84·2; H, 12·5%]. The infrared absorption curve in CCl_4 showed a strong band at 1660 cm.$^{-1}$ attributable to a C=N stretching vibration (cf. Haworth, Lunts, and McKenna [7]). Acetylation with acetic anhydride in ether gave 2β-*acetamidocholestane*, double m. p. 117—118° and 148—150° (from methanol), $[\alpha]_D$ +27·5° (*c* 1·0) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 80·8; H, 11·5. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-4α-ylamine.—Cholestan-4-one oxime {m. p. 221—223°, $[\alpha]_D$ +124° (*c* 1·5); Windaus [8] recorded m. p. 205°} (500 mg.) in refluxing butan-1-ol (50 c.c.) was treated with sodium until a saturated solution was formed. The product was a solid (453 mg.) which was chromatographed on aluminium oxide (12 g.). Successive elution with ether–benzene (1 : 1) and ether gave a solid (361 mg.) which by crystallisation from ethyl acetate afforded *cholestan-4α-ylamine*, m. p. 96—98°, $[\alpha]_D$ +10·5° (*c* 0·95) [Found (after drying at 20°/0·03 mm. for 16 hr.): C, 83·4; H, 12·3. $C_{27}H_{49}N$ requires C, 83·7; H, 12·65%]. With acetic anhydride in ether it gave *4α-acetamidocholestane*, m. p. 228—230° (from ethyl acetate), $[\alpha]_D$ +36° (*c* 0·9) [Found (after drying at 100°/0·03 mm. for 5 hr.): C, 81·0; H, 12·0. $C_{29}H_{51}ON$ requires C, 81·05; H, 11·95%].

Cholestan-4β-ylamine.—Cholestan-4-one oxime (180 mg.) in acetic acid (50 c.c.) was shaken in hydrogen with platinum oxide (50 mg.). Uptake of hydrogen was complete in 10 min. Isolation of the product in the usual manner gave an oil which was chromatographed on aluminium oxide (5 g.). Elution with ether and methylene dichloride gave an oily solid (140 mg.) which by distillation at 220°/0·01 mm. furnished cholestan-4β-ylamine, $[\alpha]_D$ +60° (*c* 1·0). Acetylation with acetic anhydride in ether at 15° gave a solid which was chromatographed on aluminium oxide. Elution with benzene gave a solid which by crystallisation from acetone afforded 4β-*acetamidocholestane*, m. p. 190—193°, $[\alpha]_D$ +33° (*c* 1·0) [Found (after drying at 100°/0·03 mm. for 5 hr.): C, 81·0; H, 11·9%].

Cholestan-7β-ylamine.—Cholestan-7-one oxime (m. p. 168—172°; 7·1 g.) in refluxing butan-1-ol (500 c.c.) was treated with sodium (50 g.) during 3 hr. The solution was worked up in the usual manner and basic material isolated as the ether-insoluble hydrochloride, which on treatment with 2N-potassium hydroxide afforded cholestan-7β-ylamine as an oil (2·88 g.), $[\alpha]_D$ +40° (*c* 3·3). Acetylation with acetic anhydride in pyridine gave a solid which on crystallisation from ether–acetone yielded 7β-*acetamidocholestane* as needles, m. p. 148—150°, $[\alpha]_D$ +61° (*c* 1·27) [Found (after sublimation at 180°/0·01 mm.): C, 80·8; H, 11·9; N, 3·4%]. Benzoylation with benzoyl chloride–pyridine at 20° for 16 hr. gave an oil which after chromatography on aluminium oxide gave a solid which on crystallisation from acetone yielded 7β-*benzamido*-*cholestane* as needles, m. p. 174—177°, $[\alpha]_D$ +81° (*c* 0·6) [Found (after drying at 20°/0·01 mm.

[7] Haworth, Lunts, and McKenna, *J.*, 1955, 986.
[8] Windaus, *Ber.*, 1920, **53**, 488.

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for 18 hr.): C, 82·9; H, 10·4. $C_{34}H_{53}ON$ requires C, 83·0; H, 10·8%]. The *hydrochloride* prepared in the usual way had m. p. 252—234° [Found (after drying at 110°/0·01 mm. for 4 hr.) C, 76·4; H, 11·9; N, 3·2. $C_{27}H_{50}NCl$ requires C, 76·4; H, 11·9; N, 3·3%].

Cholestan-7α-ylamine and Cholestan-7β-ylamine.—(*a*) Cholestan-7-one oxime (3·3 g.) in ethanol (100 c.c.) was hydrogenated at 20° in the presence of platinum oxide (200 mg.). Working up in the usual way gave the base hydrochlorides as a solid, m. p. 268—276° (424 mg.). Basification with 2N-potassium hydroxide gave an oil which partly crystallised at −20° and yielded cholestan-7α-ylamine as needles (204 mg.), m. p. *ca.* 15°, $[\alpha]_D$ −20° (*c* 1·33). The mother-liquors consisted of an uncrystallisable oil (170 mg.), $[\alpha]_D$ +54° (*c* 0·83), probably mainly the 7β-epimeride. Acetylation of cholestan-7α-ylamine with acetic anhydride–pyridine overnight gave *7α-acetamidocholestane* as needles, m. p. 216—218° (from ether), $[\alpha]_D$ +40° (*c* 0·42) [Found (after sublimation at 190°/0·01 mm.): C, 80·9; H, 11·9%].

(*b*) Cholestan-7-one oxime (1 g.) was treated with lithium aluminium hydride (250 mg.) in refluxing ether for 6 hr. The solution, worked up in the usual way, gave an oil (910 mg.) which was chromatographed on aluminium oxide (30 g.). Successive elution with ether and chloroform gave an oil (300 mg.), $[\alpha]_D$ −20° (*c* 1·0) which on acetylation with acetic anhydride in ether yielded 7α-acetamidocholestane, m. p. 216—218°, whilst use of methylene dichloride afforded an oil (610 mg.), $[\alpha]_D$ +54° (*c* 2·1), which on acetylation gave 7β-acetamidocholestane, m. p. 148—150°.

3β-Hydroxycholest-5-en-7α- and -7β-ylamine.—The amine mixture was prepared according to Eckhardt's directions [5] except that propan-1-ol was substituted for ethanol, the yield being 48%. Separation of the isomers by the method of Barnett, Ryman, and Smith [6] gave 3β-hydroxycholest-5-en-7α-ylamine, m. p. 183—185°, $[\alpha]_D$ −348° (*c* 1·6) (18%), and 3β-hydroxycholest-5-en-7β-ylamine, m. p. 196—198°, $[\alpha]_D$ +205° (*c* 1·9) (30%) (Barnett *et al.*[6] give m. p. 183—185°, $[\alpha]_D$ −327°, and m. p. 198—199°, $[\alpha]_D$ +181°, respectively).

3β-Hydroxycholestan-7α-ylamine.—3β-Hydroxycholest-5-en-7α-ylamine (1·08 g.) in acetic acid (25 c.c.) was hydrogenated at 20° in the presence of platinum oxide (300 mg.). Uptake of hydrogen was completed in 5 min. and the product on crystallisation from ether–acetone gave 3β-hydroxycholestan-7α-ylamine, m. p. 158—162°, $[\alpha]_D$ −18° (*c* 1·2) (Barnett *et al.*[6] give m. p. 87—89°, $[\alpha]_D$ −143°). Acetylation with acetic anhydride in ether at 15° gave a solid which on crystallisation from methanol furnished *7α-acetamidocholestan-3β-ol*, needles, m. p. 270—272°, $[\alpha]_D$ −9° (*c* 1·3) [Found (after drying at 120°/0·005 mm. for 4 hr.): C, 78·1; H, 11·2; N, 3·2. $C_{29}H_{51}O_2N$ requires C, 78·1; H, 11·5; N, 3·1%].

3β-Hydroxycholestan-7β-ylamine.—3β-Hydroxycholest-5-en-7β-ylamine (1·8 g.) in glacial acetic acid (43 c.c.) was shaken with hydrogen in the presence of platinum oxide (300 mg.). Uptake of hydrogen was complete in 10 min. The product was an uncrystallisable oil (1·86 g.), $[\alpha]_D$ +44° (*c* 3·0). Acetylation in ether with acetic anhydride at 15° for 16 hr. gave a solid which on crystallisation from acetone–methanol gave *7β-acetamidocholestan-3β-ol*, needles, m. p. 255—259°, $[\alpha]_D$ +63° (*c* 0·6) [Found (after drying at 120°/0·005 mm. for 4 hr.): C, 77·2; H, 11·1; N, 2·9%]. Benzoylation with benzoyl chloride–pyridine at 20° for 18 hr. gave an oil which on crystallisation form acetone gave *7β-benzamidocholestan-3β-yl benzoate*, m. p. 183—184°, $[\alpha]_D$ +31° (*c* 0·6) [Found (after drying at 90°/0·02 mm.): C, 80·7; H, 9·8. $C_{41}H_{57}O_3N$ requires C, 80·5; H, 9·4%].

3β-Hydroxycholestan-7α- and -7β-ylamine.—3β-Hydroxycholest-5-en-7-one oxime (m. p. 240—242°; 2·36 g.) in glacial acetic acid (120 c.c.) and methanol (90 c.c.) was hydrogenated in the presence of platinum oxide (317 mg.). Theoretical uptake of hydrogen was complete in 5 hr. The product, a solid, crystallised from acetone–methanol to give *3β-hydroxycholestan-7β-ylamine* which after recrystallisation from the same solvent had m. p. 184—186°, $[\alpha]_D$ +102° (*c* 0·85) (20%) [Found (after drying at 110°/0·01 mm. for 18 hr.): C, 80·4; H, 12·2; N, 3·6 $C_{27}H_{49}ON$ requires C, 80·3; H, 12·2; N, 3·5%]. Concentration of the mother-liquors gave crystals, m. p. 152—160°, which by recrystallisation from acetone gave *3β-hydroxycholestan-7α-ylamine*, m. p. 156—158°, $[\alpha]_D$ −24° (*c* 1·3) (28%) [Found (after drying at 110°/0·01 mm. for 18 hr.): C, 80·3; H, 12·2; N, 3·6%].

Cholesta-3 : 5-dien-7-one Oxime.—Cholesta-3 : 5-dien-7-one was oximated with hydroxylamine acetate in refluxing ethanol. The product on crystallisation from methanol gave cholesta-3 : 5-dien-7-one oxime as plates, m. p. 178—180°.

Cholest-4-en-7β-ylamine.—Cholesta-3 : 5-dien-7-one oxime (6 g.) in refluxing ethanol (420 c.c.) was treated with sodium (36 g.). The solution was worked up in the usual manner, and basic

material was isolated as the ether-insoluble hydrochloride, m. p. 245—252° (2·7 g.). Basification with ammonia gave cholest-4-en-7β-ylamine as an oil (2·5 g.), $[\alpha]_D$ +85° (*c* 2·8). Acetylation with acetic anhydride–pyridine at 20° for 24 hr., followed by chromatography on aluminium oxide gave, by elution with benzene–pentane (1 : 4), 7β-*acetamidocholest-4-ene*, double m. p. 150—152° and 197—198°, $[\alpha]_D$ +58° (*c* 1·43) [Found (after sublimation at 180°/0·01 mm.): C, 81·1; H, 11·5. $C_{29}H_{49}ON$ requires C, 81·3; H, 11·6%]. Benzoylation with benzoyl chloride–pyridine at 20° for 48 hr. followed by chromatography on aluminium oxide gave by elution with pentane a solid which on crystallisation from acetone afforded 7β-*benzamidocholest-4-ene* as needles, m. p. 190—192°, $[\alpha]_D$ +80° (*c* 1·12) [Found (after drying at 110°/0·01 mm. for 4 hr.): C, 83·1; H, 10·6. $C_{34}H_{51}ON$ requires C, 83·4; H, 10·5%].

One of us (R. J. W. C.) thanks the Department of Scientific and Industrial Research, and another (D. E. E.) Monsanto Chemicals Ltd., for financial support. Glaxo Laboratories Ltd. are thanked for a gift of cholesterol.

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874. *Solutions of Alcohols in Non-polar Solvents. Part IV.* Some Thermodynamic Properties of Glycols in Benzene, Heptane, and* cyclo*-Hexane.*

By L. A. K. STAVELEY and G. L. MILWARD.

Measurements have been made by the synthetic method, over a range of temperature, of the solubilities of five glycols in benzene, heptane, and *cyclo*hexane. The heats of solution ΔH and the standard entropies of solution $\Delta S°$ have been evaluated; in any one solvent there is a linear relation between ΔH and $\Delta S°$.

Specificity in the relation between solute and solvent molecules is shown by there being no uniform trend in solubility with increasing molecular weight of the glycol in any solvent. Moreover, the dependence of both ΔH and $\Delta S°$ on the number of carbon atoms in the glycol molecule " alternates," *i.e.*, a large increment in ΔH or $\Delta S°$ on passing from one glycol to the next is followed by a smaller one, and *vice versa*. The steps which give the larger increments in heptane solutions produce the smaller increments in benzene and *cyclo*hexane. A possible explanation of the effect for the heptane solutions is advanced.

PREVIOUS papers of this Series concerned dilute solutions of primary alcohols in non-polar solvents. Certain properties of these solutions reveal specificity in the solute–solvent relation. Thus measurements of their viscosity [1] and the heat of solution of water in them [2] indicated that the molecules of alcohols from butanol or pentanol onwards, when dissolved in benzene, tend to adopt a cyclic configuration with partial screening of the hydroxyl group, while the values of the partial molar volumes of the alcohols at infinite dilution " alternate " in benzene and *cyclo*hexane, but not in heptane,[3] as the homologous series is ascended. We have now investigated solutions where the solute molecules have polar groups at each end, interaction between which will influence the relative stabilities of different molecular configurations. The solutes chosen have been the first five polymethylene glycols $HO\cdot[CH_2]_n\cdot OH$, whose solubility we measured in benzene, heptane, and *cyclo*hexane as a function of temperature. These solubilities are so small that the solutions can be regarded as ideal, allowing values of the heat and entropy of solution to be derived.

* Part III, Staveley and Taylor, *J.*, 1956, 200.

[1] Staveley and Taylor, *J.*, 1956, 200.
[2] Staveley, Johns, and Moore, *J.*, 1951, 2516.
[3] Staveley and Spice, *J.*, 1952, 406.

XUM

Experimental

Solubilities were determined by the synthetic method.[2,4] Known masses of solute (from a weight pipette) and solvent were introduced into a glass tube (capacity *ca.* 25 ml. in experiments with benzene, and *ca.* 60 ml. with heptane and *cyclo*hexane) which was then sealed and heated until the contents became homogeneous. As it cooled slowly the temperature at which the two phases separated (the " cloud-point ") was determined. Care was taken to exclude moisture during filling. Numerous determinations were made of the cloud-point with each tube, and an average taken. Deviations of individual values from the mean seldom exceeded $\pm 0{\cdot}2°$ for benzene solutions and $\pm 0{\cdot}4°$ for heptane and *cyclo*hexane.

Doubts about the reliability of the synthetic method were expressed by Joris and Taylor,[5] who, using tritium as tracer, obtained a markedly lower value for the solubility of water in benzene. Recently, however, Wing and Johnson,[6] also radiochemically, have obtained a value in good agreement with that found by the synthetic method, so there seems no reason to distrust its reliability for the determination of the solubility of one liquid in another even when the solubility is small.

Ethylene, trimethylene, and pentamethylene glycols were dried (Na_2SO_4) and then fractionated at atmospheric pressure. Tetramethylene and hexamethylene glycols were fractionally crystallized, the former then being distilled *in vacuo*. B. p.s (corr. to 760 mm.) or f. p.s of the glycols were as follows: ethylene, b. p. 196·8°; trimethylene, b. p. 214·0—214·4°; tetramethylene, f. p. 18·7°; pentamethylene, b. p. 240·2—241·8°; hexamethylene, f. p. 41·6°. The three solvents were as pure as those used earlier,[3] and were all finally dried by distillation from phosphoric oxide.

Table 1. *Solubility of glycols* (N = *mole fraction in benzene,* cyclo*hexane, and heptane*).

Ethylene		Trimethylene		Tetramethylene		Pentamethylene		Hexamethylene	
				Benzene					
10^3N	t	10^3N	t	10^3N	t	10^3N	t	10^3N	t
2·51	29·0	2·92	26·2	3·01	27·0	3·33	31·5	7·00	43·8
4·79	47·1	5·23	42·1	4·49	36·4	4·36	37·6	9·81	51·9
6·71	56·8	7·16	51·0	6·97	47·3	6·49	47·5	12·97	58·5
9·43	67·4	10·09	60·7	10·75	58·7	8·20	52·8	14·72	61·4
		11·73	66·2						
$a = 6{\cdot}5108$		$6{\cdot}6347$		$7{\cdot}2734$		$7{\cdot}4774$		$8{\cdot}0476$	
$b = 1{\cdot}5452$		$1{\cdot}5482$		$1{\cdot}7396$		$1{\cdot}8142$		$1{\cdot}9669$	
				cyclo*Hexane*					
0·380	46·1	0·283	39·3	0·192	33·2	0·292	40·9	0·359	41·1
0·490	51·8	0·635	54·4	0·348	44·1	0·788	59·2	0·675	53·1
0·816	62·9	0·9645	63·9	0·651	56·7	1·074	65·6	1·186	64·1
1·065	67·7	1·219	68·3	1·179	68·4	1·486	74·2	1·414	67·3
1·418	75·2	1·297	69·4						
$a = 7{\cdot}5223$		$7{\cdot}6851$		$7{\cdot}9097$		$7{\cdot}9224$		$8{\cdot}2208$	
$b = 2{\cdot}2181$		$2{\cdot}2568$		$2{\cdot}3369$		$2{\cdot}3386$		$2{\cdot}4092$	
				Heptane					
0·344	42·7	0·244	39·5	0·2785	39·3	0·401	46·2	0·476	45·6
0·408	47·0	0·500	50·1	0·3795	44·8	0·491	49·9	0·501	46·7
0·448	49·7	0·771	58·6	0·385	45·0	0·754	58·0	0·664	51·2
0·672	56·6	1·027	64·6	0·5645	52·7	1·095	65·6	1·152	62·6
0·864	63·4			0·927	62·9			1·522	68·0
1·029	67·9								
$a = 7{\cdot}1772$		$7{\cdot}8840$		$7{\cdot}8327$		$8{\cdot}2368$		$8{\cdot}3308$	
$b = 2{\cdot}1001$		$2{\cdot}3212$		$2{\cdot}3067$		$2{\cdot}4372$		$2{\cdot}4386$	

Results are recorded in Table 1. N is the mole fraction of the glycol in a saturated solution at the " cloud-point," $t°$ c. For every solution, $\log_{10}N$ was linear with $1/T$, where $T = t + 273{\cdot}1°$. Values of a and b in the equation $\log_{10}(10^4N) = a - 10^3b/T$ were evaluated for each system by the method of least squares, and are given in Table 1.

[4] Staveley, Jeffes, and Moy, *Trans. Faraday Soc.*, 1943, **39**, 5.
[5] Joris and Taylor, *J. Chem. Phys.*, 1948, **16**, 45.
[6] Wing and Johnson, *J. Amer. Chem. Soc.*, 1957, **79**, 86

Some rough measurements were also made of the solubility of the three hydrocarbons in ethylene glycol, and of benzene and *cyclo*hexane in pentamethylene glycol. Values of x, the mole fraction of the hydrocarbon, were: (1) in ethylene glycol, for benzene $x = 0{\cdot}04$ at 53°, for *cyclo*hexane $x < 0{\cdot}014$ at 100°, for heptane $x < 0{\cdot}003$ at 100°; (2) in pentamethylene glycol, for benzene $x = 0{\cdot}38$ at 87° and 0·30 at 57°, for *cyclo*hexane $x = 0{\cdot}10$ at 70°.

Discussion

The existence of marked specificity in the relations between glycol and hydrocarbon molecules is apparent on comparing plots of log N against $1/T$ for the several glycols in a given solvent, or on considering the solubilities of the glycols in the same solvent at a given temperature. In Table 2 the solubilities are given at 39·4° ($10^3/T = 3{\cdot}2$). In no solvent is there a steady increase in solubility with increasing length of the hydrocarbon chain in the glycol. For the first four glycols in *cyclo*hexane and heptane there is little change in the solubility.

Table 2. *Interpolated solubilities of glycols in benzene, heptane, and* cyclo*hexane at* 39·4° c *expressed as the mole fraction of glycol* $\times 10^4$.

	Benzene	Heptane	*cyclo*Hexane
Ethylene glycol	36·8	2·86	2·66
Trimethylene glycol	47·9	2·86	2·91
Tetramethylene glycol	50·9	2·83	2·70
Pentamethylene glycol	47·0	2·74	2·75
Hexamethylene glycol	56·9	3·37	3·25

Before the results in Table 1 can be used to give heats and entropies of solution, we must consider whether these dilute solutions of glycols in non-polar solvents can be regarded as ideal. Glycol molecules are in a sense intermediate between primary alcohol molecules and water molecules. Wolf [7] has shown that at room temperature primary alcohols are effectively unassociated in benzene up to a mole fraction of *ca.* 10^{-2}, and in hexane and *cyclo*hexane up to *ca.* 3×10^{-3} and *ca.* $1{\cdot}5 \times 10^{-3}$ respectively. These concentrations are considerably higher than the solubilities of the glycols. Water in benzene has a normal molecular weight [8] up to its solubility limit at 5·4°, and at 20° accurately obeys Henry's law to the limit of saturation,[9] when the mole fraction of water is $2{\cdot}5 \times 10^{-3}$. This is roughly the same as the solubility of the glycols in benzene at the same temperature. Therefore it is reasonable to suppose that in the present solutions the glycols behave as unassociated, ideal solutes. If it is further supposed that the glycol-rich phase which separates from a saturated solution is pure glycol, the heat of solution ΔH and the entropy of solution ΔS can be readily evaluated from the slope and intercept respectively of the plot of log N against $1/T$. For the evaluation of the entropy of solution we shall take as the standard solution an ideal supersaturated solution of unit molality, when the entropy increase $\Delta S°$ per mole of glycol on passing from the pure liquid to the standard solution is given by $\Delta S° = 4{\cdot}573\,[a - 4 + \log_{10}(1 + 1000/M)]$, where M is the molecular weight of the solvent and a, as defined above, determines the intercept of $\log_{10}10^4N$ with $10^3/T$. The heat of solution (to give the ideal dilute solution) is given by $\Delta H = 4{\cdot}573b$, where b is the slope of the same plot. Values of ΔH and $\Delta S°$ are given in Table 3. Since the glycol-rich phase can never be quite pure, a correction involving the temperature variation of the composition of the glycol-rich phase should be applied, but the solubilities of the *cyclo*hexane and heptane in the glycol are so small that this must be negligible, and the ΔH and $\Delta S°$ values of Table 3 should be good approximations to those of pure glycols. For benzene the correction will be more important and, from the results for pentamethylene glycol, the change in ΔH on applying it might be *ca.* 1 kcal./mole. It should be less for the lower

[7] Wolf, *Trans. Faraday Soc.*, 1937, **33**, 179.
[8] Peterson and Rodebush, *J. Phys. Chem.*, 1928, **32**, 709.
[9] Greer, *J. Amer. Chem. Soc.*, 1930, **52**, 4191.

glycols. Unfortunately, only ethylene glycol was available in sufficient amount to permit the solubility of the hydrocarbon in it to be measured accurately. However, while ΔH and $\Delta S°$ of Table 3 for benzene solutions would be slightly altered if the correction could be applied, they are still useful for comparison.

TABLE 3. *Heats of solution* (ΔH, *kcal./mole*) *and entropies of solution* [$\Delta S°$, *cal./(mole deg.)*].

	Benzene		Heptane		*cyclo*Hexane	
	ΔH	$\Delta S°$	ΔH	$\Delta S°$	ΔH	$\Delta S°$
Ethylene glycol	7·07	16·70	9·60	19·29	10·14	21·18
Trimethylene glycol	7·08	17·26	10·62	22·52	10·32	21·93
Tetramethylene glycol	7·96	20·18	10·55	22·29	10·69	22·96
Pentamethylene glycol	8·30	21·12	11·15	24·14	10·69	23·01
Hexamethylene glycol	9·00	23·72	11·15	24·57	11·02	24·38

The values of ΔH for the glycols with even numbers of carbon atoms are approximately double those for the primary alcohols with half the number of carbon atoms (ΔH for alcohols has been determined calorimetrically by Wolf and his co-workers [10]), as shown in Table 4. The lower heats of solution (both of the glycols and of the alcohols) in benzene

TABLE 4. *Comparison of the molar heats of solution* (ΔH, *kcal./mole*) *of primary alcohols and glycols. The values for the alcohols refer to infinitely dilute solution.*

	Benzene	*cyclo*Hexane	Alcohol in hexane, glycol in heptane
$2\Delta H$ for $CH_3 \cdot OH$	7·0	12·4	11·4
ΔH for $(CH_2 \cdot OH)_2$	7·1	10·1	9·6
$2\Delta H$ for $C_3H_5 \cdot OH$	7·4	11·6	11·4
ΔH for $(C_3H_4 \cdot OH)_2$	8·0	10·7	10·6
$2\Delta H$ for $C_3H_7 \cdot OH$	7·7	—	11·3
ΔH for $(C_3H_6 \cdot OH)_2$	9·0	11·0	11·2

than in heptane and *cyclo*hexane are evidence of the stronger interaction of the hydroxyl groups with benzene molecules than with the other hydrocarbon molecules. This stronger interaction leads to more pronounced solvation with its accompanying entropy loss and hence accounts for the smaller $\Delta S°$ values in benzene. But in their effect on the solubility, the smaller ΔH values in benzene have a larger influence than the smaller $\Delta S°$ values, so that the solubilities of the glycols in benzene are considerably larger than in the other solvents.

While Wolf's figures show a decrease in ΔH for the primary alcohols with increasing chain length in hexane, and an increase in benzene, for the glycols ΔH increases with increasing chain length in all three solvents. And whereas the trend in ΔH with the primary alcohols is irregular, for the glycols it shows an interesting alternation (Fig. 1). The same effect is shown by $\Delta S°$ (Fig. 2). A large increment in ΔH or $\Delta S°$ is followed by a smaller one, and *vice versa*, and small though some of these increments are, this is true for all twenty-four increments involved. The origin of this alternation could reside, *a priori*, in the nature of the pure liquid glycols, or in that of the solutions, or both. The m. p.s of the solids show an alternation, so that if the liquids are considered at a fixed temperature then there is an alternation in the separation of this temperature from the m. p. However, the physical properties (even molar volumes) of the glycols have not been sufficiently studied to provide evidence of any alternation. That the steps which produce the *larger* increments in ΔH and $\Delta S°$ in benzene and *cyclo*hexane solutions (such as that from trimethylene to tetramethylene glycol) give the *smaller* ones in heptane strongly suggests that the observed alternations in ΔH and $\Delta S°$ depend partly on the nature of the solute–solvent interactions.

These interactions may be simplest when heptane is the solvent, since then the solute

[10] Wolfe, Pahlke, and Wehage, *Z. phys. Chem.*, 1935, *B*, **28**, 1.

FIG. 1.

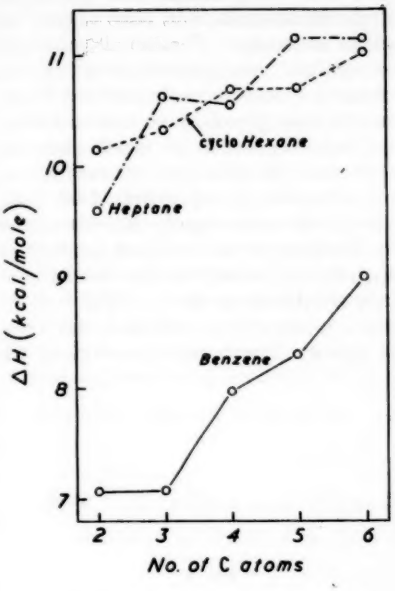
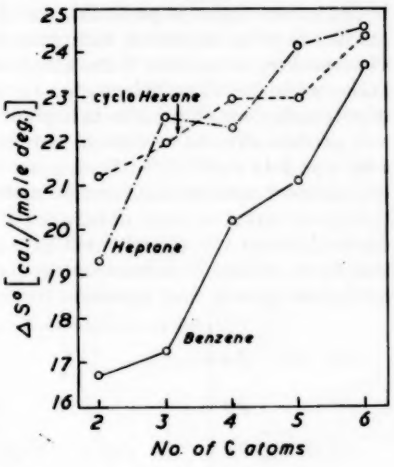


FIG. 2.



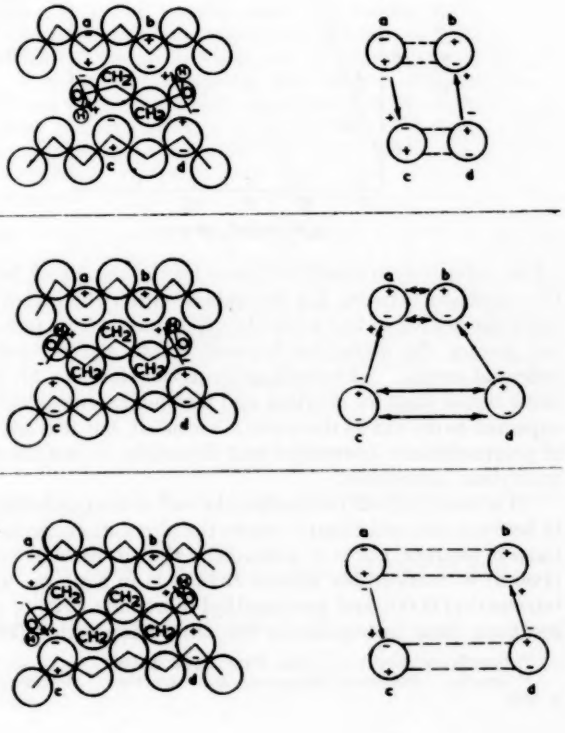


FIG. 3. *Possible idealized arrangements of the molecules of (from top to bottom) ethylene, trimethylene, and tetramethylene glycol in solution in heptane.*

and solvent alike have flexible zig-zag chains, and it seems probable that (owing to dispersion forces and short-range repulsion forces) glycol molecules will tend to pack as economically as possible into the surrounding heptane molecules. Parallel alignment of hydrocarbon chains is preferred, and Fig. 3 shows idealized arrangements in which two parallel heptane molecules with stretched chains have a glycol molecule between them. Close-packing is assisted if the ethylene and tetramethylene glycols have *trans*-configurations while the trimethylene glycol is *cis*. This has some support in the dipole moments of polymethylene dibromides in heptane, which for ethylene, trimethylene, tetramethylene, and pentamethylene dibromide also show an alternation, being respectively 1·02, 2·02, 1·96, and 2·44 D at 25°.[11] Each polar $-CH_2 \cdot OH$ group will induce dipoles in segments of the adjacent surrounding heptane molecules. The direction of the resultant moment of this group makes an angle of between 61° and 67° with the C–O bond,[12] so that the induced dipoles lettered a, b, c, and d will have approximately the directions shown. Fig. 3 shows that there is attraction between the pairs of dipoles a–b and c–d for ethylene and tetramethylene glycols, but repulsion for trimethylene glycol. The potential energy of the

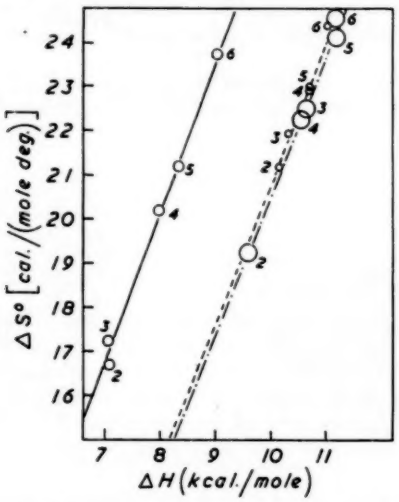


FIG. 4.

Large circles, heptane; medium circles, benzene; small circles, *cyclo*hexane. Numerals refer to the number of carbon atoms in the glycol molecules.

solute–solvent system will be higher for the last glycol, both because of this and because of the repulsion between the *cis*-dipoles within the glycol molecule. The heat of solution, being the heat absorbed when the glycol passes from pure liquid to solution, will be smaller the greater the attraction between solute and solvent molecules and the lower their potential energy. This could account, therefore, for ΔH for trimethylene glycol in heptane being higher than for ethylene and tetramethylene glycol. The alternation would then be expected to die out as the series is ascended, but it is noteworthy that the dipole moments of polymethylene dibromides and dicyanides do not reach a steady value below the hexamethylene compounds.

It is more difficult to visualise the sort of intermolecular relation which may be preferred in benzene and *cyclo*hexane, where the alternation effects in ΔH and $\Delta S°$ are the reverse of those in heptane, but it is noteworthy that in benzene the moment of ethylene dibromide (1·50 D) is considerably greater than it is in heptane, whereas those of trimethyl (1·97), tetramethyl (2·00), and pentamethyl dibromide (2·25 D) are respectively less, greater, and less than those in heptane at the same temperature (25°).[11] Thus benzene may favour

[11] Smyth and Walls, *J. Chem. Phys.*, 1933, **1**, 200.
[12] Smyth, "Dielectric Behaviour and Structure," McGraw-Hill Book Co., Inc., New York, 1955, p. 302.

somewhat the adoption of *cis* (or skew) polar configurations of the glycol molecules with an even number of carbon atoms. Since the geometry of the benzene molecules has less affinity with that of glycol molecules than that of either heptane or *cyclo*hexane molecules, it might be expected that as the glycol chain lengthens and its polar ends (and the effects that they induce) become more independent, any particular configuration of the solute molecules should be less preferred and consequently the entropy of solution should be correspondingly increased. In fact, $\Delta S°$ increases more rapidly with increasing chain length of the glycol in benzene than it does in either heptane or *cyclo*hexane. If $\Delta S°$ were corrected to allow for the impurity of the glycol phase (p. 4371), then the approximate results for the composition of the glycol-rich phase obtained for ethylene and pentamethylene glycol indicate that the corrected $\Delta S°$ values for benzene solutions would show an even more rapid increase with increasing glycol chain length.

Finally, Fig. 4 shows that these solutions provide further examples of systems in which the relation between the heat and entropy of solution for a series of solutes in a given solvent is linear. All three lines have approximately the same slope, but that for benzene is displaced very considerably from the other two, which fall very close together.

INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, June 13th*, 1957.]

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875. N-*Oxides and Related Compounds. Part V.* The Tautomerism of* 2- *and* 4-*Amino- and -Hydroxy-pyridine* 1-*Oxide.*

By J. N. GARDNER and A. R. KATRITZKY.

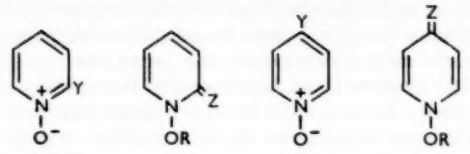
The basicities of the oxides named in the title and alkylated derivatives of their tautomers show that the 2- and 4-amino-compounds exist as such; the 4-hydroxy-compound is a mixture of comparable amounts of both tautomers in aqueous solution but the method fails with 2-hydroxypyridine 1-oxide. Previous work is reviewed. Ultraviolet and infrared evidence supports these conclusions and shows that 2-hydroxypyridine 1-oxide exists as strongly hydrogen-bonded 1-hydroxypyrid-2-one. The 2-amino-1-methoxypyridinium cation comes rapidly into equilibrium with hydroxyl ion; slow decomposition to 2-aminopyridine competes with this. The measured tautomeric constants are compared with those of the corresponding pyridines.

THE tautomerism of 2- and 4-amino- and 2- and 4-hydroxy-pyridine 1-oxide (I and III; Y = NH_2 or OH) with the alternative 1-hydroxypyridone imine and 1-hydroxypyridone forms (II and IV; R = H, Z = NH or O), has already been much investigated.[1-8] But in all cases where a decision was reached objections can be raised to its validity, as discussed below. Therefore the basicities of the parent compounds have been compared with those of alkylated derivatives of both forms, not only to find the predominant tautomer at equilibrium, but also to measure the stability difference between the forms,[9,10] and to compare the results with the published [10,11] information in the pyridine series.

* Papers by Katritzky (*J.*, 1956, 2063, 2404; 1957, 191) and by Katritzky, Randall, and Sutton (*J.*, 1957, 1769) are regarded as Parts I, II, III, and IV, respectively, of this series.

[1] Ochiai and Hayashi, *J. Pharm. Soc. Japan*, 1947, **67**, 151; *Chem. Abs.*, 1951, **45**, 9540; cf. Hayashi, *J. Pharm. Soc. Japan*, 1951, **71**, 213 (in German).
[2] Shaw, *J. Amer. Chem. Soc.*, 1949, **71**, 67.
[3] Cunningham, Newbold, Spring, and Stark, *J.*, 1949, 2091.
[4] Hirayama and Kubota, *J. Pharm. Soc. Japan*, 1953, **73**, 140; *Chem. Abs.*, 1953, **47**, 4196.
[5] Jaffe, *J. Amer. Chem. Soc.*, 1955, **77**, 4445.
[6] *Idem, ibid.*, p. 4448.
[7] Costa, Blasina, and Sartori, *Z. phys. Chem.* (*Frankfurt*), 1956, **7**, 123.
[8] Katritzky, *J.*, 1957, 191.
[9] Tucker and Irvin, *J. Amer. Chem. Soc.*, 1951, **73**, 1923.
[10] Angyal and Angyal, *J.*, 1952, 1461.
[11] Albert and Phillips, *J.*, 1956, 1294.

Preparation of Compounds.—Reduction of 4-nitropyridine 1-oxide gave 4-amino-pyridine 1-oxide,[12] converted by methyl toluene-*p*-sulphonate into a quaternary salt



(I) (II) (III) (IV)

which with perchloric acid gave 4-amino-1-methoxypyridinium perchlorate. 4-Chloro-pyridine 1-oxide with mono- and di-methylamine gave 4-mono- and 4-di-methylamino-pyridine 1-oxide; the latter was converted into quaternary salts as above.

Compounds in the 2-amino-series were prepared by known [8] methods, as were those of the 4-hydroxy-series,[2,13] except that 1-methoxypyrid-4-one was obtained from 4-hydroxy-pyridine 1-oxide with sodium methoxide and methyl toluene-*p*-sulphonate.

2-Chloropyridine 1-oxide with sodium benzyloxide gave 1-benzyloxypyrid-2-one as the only product isolated, instead of the expected 2-benzyloxypyridine 1-oxide. Shaw reported [2] that the latter was partially isomerised by hydrochloric acid. Catalytic reduction of 1-benzyloxypyrid-2-one gave 2-hydroxypyridine 1-oxide. However, with sodium methoxide and ethoxide, 2-chloropyridine 1-oxide gave the 2-methoxy- and the 2-ethoxy-compound as expected. 1-Methoxypyrid-2-one was prepared as for the 4-isomer above.

Results.—The pK values in Table 1 were determined by potentiometric titration, except for values below *ca.* 2 where the spectrometric method was used. Table 1 also

TABLE 1.

Compound	pK_a	Spread (±)	Concn. (M)	Wave-length [e] (mμ)	pK_a of corresp. pyridine	pK_a less pyridine pK_a
4-Aminopyridine 1-oxide	3·69 [b]	0·03	0·0083	—	9·17 [f]	−5·48
4-Methylaminopyridine 1-oxide	3·85	0·03	0·0074	—	—	—
4-Dimethylaminopyridine 1-oxide	3·88	0·07	0·0077	—	—	—
4-Amino-1-methoxypyridinium perchlorate [a]	>11	—	0·0075	—	12·5 [f]	*ca.* 0
4-Dimethylamino-1-methoxypyridinium perchlorate [a]	>11	—	0·0073	—	—	—
2-Aminopyridine 1-oxide	2·67	0·04	0·096	—	6·86 [f]	−4·19
2-Methylaminopyridine 1-oxide	2·61	0·07	0·0088	—	—	—
2-Dimethylaminopyridine 1-oxide	2·27	0·08	0·011	—	—	—
2-Amino-1-methoxypyridinium perchlorate [a]	12·4 [c]	—	—	—	12·2 [f]	*ca.* 0
2-Methylamino-1-methoxypyridinium toluene-*p*-sulphonate [a]	>11	—	0·0086	—	—	—
4-Hydroxypyridine 1-oxide	2·45 [d]	0·03	0·096	—	3·27 [g]	—
4-Methoxypyridine 1-oxide	2·05	0·06	0·097	—	6·62 [g]	−4·57
4-Benzyloxypyridine 1-oxide	1·99	0·05	0·095	—	—	—
1-Methoxypyrid-4-one	2·57	0·08	0·092	—	3·33 [g]	−0·76
1-Benzyloxypyrid-4-one	2·58	0·05	0·095	—	—	—
2-Hydroxypyridine 1-oxide	−0·8	0·2	$9·6 \times 10^{-5}$	295	0·75 [g]	—
2-Methoxypyridine 1-oxide	1·23	0·08	$7·1 \times 10^{-5}$	247	3·28 [g]	−2·05
2-Ethoxypyridine 1-oxide	1·18	0·18	$7·1 \times 10^{-5}$	247	—	—
1-Benzyloxypyrid-2-one	−1·7	0·1	$5·5 \times 10^{-5}$	295	—	—
1-Methoxypyrid-2-one	−1·3	0·2	$1·2 \times 10^{-4}$	300	0·32 [g]	−1·53

[a] Values for these compounds refer to back-titrations with alkali. [b] Lit.,[14] 3·65,[4] 3·54. [c] See text. [d] Lit.,[14] 2·36. [e] An entry in this column signifies that the determination was spectrometric (otherwise potentiometric). [f] Ref. 10. [g] Ref. 11.

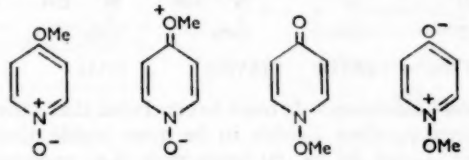
gives the initial concentration of the base from which thermodynamic pK values can be calculated (cf. ref. 11). Values for 1-methoxypyrid-2- and -4-one imines were obtained by

[12] Cf. Kato, Hamaguchi, and Oiwa, *Pharm. Bull.* (*Japan*), 1956, **4**, 178.
[13] Ochiai, *J. Org. Chem.*, 1953, **18**, 534.
[14] Jaffe and Doak, *J. Amer. Chem. Soc.*, 1955, **77**, 4441.

back-titration of the corresponding 1-methoxy-2- and -4-aminopyridinium salts, as the former compounds could not be isolated.

In the 2- and the 4-amino-series, if it is assumed that the true basicities of the separate tautomeric forms (*e.g.*, 2-aminopyridine 1-oxide and 1-hydroxypyrid-2-one imine) are unchanged by *O*- or *N*-alkylation, the above results show [10,11] that the amino-forms are preferred by factors of at least 10^8 and 10^7 respectively, which are far too large to be materially affected by the above assumption.

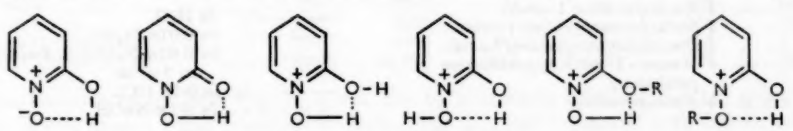
In the 4-hydroxy-series, qualitatively the results show that there can be little difference in stability between the hydroxy- and the pyridone forms. Quantitatively, interpretation



(V) (VI) (VII) (VIII)

is more difficult: as the pK of 4-methoxypyridine 1-oxide is *lower* than that of 4-hydroxypyridine 1-oxide, the methyl group in the former must (whatever the tautomeric composition of the latter) have a base-weakening effect. The pK's of aniline and hydroxy- and methoxy-aniline show (see discussion in ref. 11) that, whereas the inductive effects are approximately equal, the mesomeric effect of hydroxyl is considerably more base-strengthening than is that of methoxyl (by about 0·3 pK unit in *o*- and *p*-substituted anilines). The two main canonical forms of 4-methoxypyridine 1-oxide are (V) and (VI), those of 1-methoxypyrid-4-one are (VII) and (VIII), showing that mesomerism involving the methoxyl group is much more important in the former compound where the methyl group can be expected to exert a considerable base-weakening effect. Thus the intrinsic pK of the 1-hydroxypyrid-4-one tautomer should be close to the homologue value of 2·57, but the 4-hydroxy-tautomer should be more strongly basic than 4-methoxypyridine 1-oxide (pK 2·05) by at least 0·3 units. It is concluded that 4-hydroxypyridine 1-oxide exists in aqueous solution as a mixture of comparable amounts of *N*-oxide and pyridone forms.

The 2-hydroxy-series is still more complicated. In whichever form it exists, 2-hydroxypyridine 1-oxide will be strongly hydrogen-bonded (IX or X) (see below and compare tropolone [15]). In addition (in distinction to the 2-amino-series) there are two possible structures for the protonated species (XI and XII). The pK values of the alternative alkylated derivatives show that (XIV) can lose its proton more readily than (XIII); this probably indicates that form (XI) is more stable than (XII) (although it is the loss of a

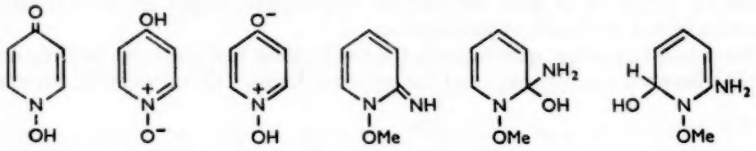


(IX) (X) (XI) (XII) (XIII) (XIV)

different proton), but (XI) may lose a proton to give either (IX) or (X). The stability of the hydrogen bond in (IX or X) may be obtained by considering how much more readily (XI) loses its proton than (XIII). Using $\Delta F = -RT \ln K$, we find ΔF to be *ca.* 3 kcals./mole. The above conclusions will now be compared with evidence on the position of tautomerism that has been obtained in other ways.

The Hammett Equation.—Jaffe [5] calculated that the intrinsic pK's of 4-hydroxy- and 4-amino-pyridine 1-oxide, existing as such, would be 1·68 and 2·22, both values being considered to be low because of uncertainties in the σ values for OH and NH_2 to be used in

the Hammett equation. He measured the actual pK's as 2·36 and 3·65 (cf. Table 1) and concluded (very unconvincingly) that this showed that 4-hydroxypyridine 1-oxide existed as such and not as 1-hydroxypyrid-4-one, and that 4-aminopyridine 1-oxide existed either as such or possibly as an equilibrium mixture with the pyridone imine (the latter was considered less probable on grounds of resonance and bond energies).

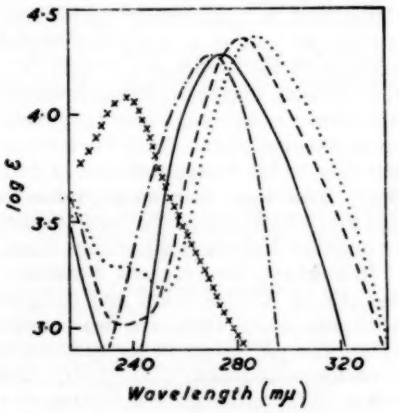


(XV) (XVI) (XVII) (XVIII) (XIX) (XX)

The Molecular-orbital Calculation.—It must be concluded that Jaffe's calculation [6] which showed 2- and 4-hydroxypyridine 1-oxide to be more stable than the corresponding 1-hydroxypyrid-2- and -4-ones by *ca.* 20 kcals./mole (*i.e.*, corresponding to a ratio of *ca.* 10^{14} between the forms) was not sufficiently refined.

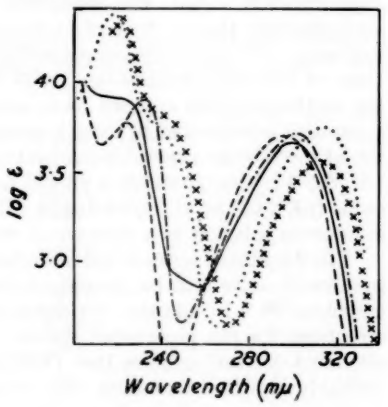
Hirayama and Kubota [4] appear to have deduced from resonance-energy considerations that 4-aminopyridine 1-oxide exists as such.

FIG. 1. *Solvent*: 0·1N-*sodium hydroxide.*



——— 4-*Aminopyridine* 1-*oxide.*
— — — — 4-*Methylaminopyridine* 1-*oxide.*
. . . . . 4-*Dimethylaminopyridine* 1-*oxide.*
— · — · — 4-*Amino*-1-*methoxypyridinium perchlorate.*
× × × × × 4-*Aminopyridine.*

FIG. 2. *Spectrum of* 2-*hydroxypyridine* 1-*oxide.*



——— *in* H_2O.
— — — — *in* 0·01N-H_2SO_4.
. . . . . *in* 0·01N-NaOH. 2-*Aminopyridine* 1-*oxide.*
— · — · — *in* 0·1N-HCl.
× × × × × *in* 0·1N-NaOH.

Ultraviolet Spectra.—Ochiai considered [1] that, because the spectrum of 4-hydroxypyridine 1-oxide showed little change in acid or alkaline solution, there was little contribution from the pyridone form (XV) but the "benzenoid form" (XVI) and/or the "betaine form" (XVII) were important.

Shaw showed [2] that the spectra of 4-hydroxypyridine 1-oxide and both possible benzyl (also true of methyl-) derivatives were all too similar to indicate the structure of the first. Fig. 1 shows that this holds also in the 4-amino-series.

Shaw,[2] and Spring and his co-workers,[3] independently concluded that the spectra in ethanol of 2-hydroxypyridine 1-oxide and alkylated derivatives showed that the parent

existed as 1-hydroxypyrid-2-one. The dangers of measuring the absorption of acids or bases of appreciable strength in unbuffered solvents are known.[16] Fig. 2 shows the neutral molecule and anion spectra of 2-hydroxypyridine 1-oxide (lit.,[2] pK_a 5·9; we find 5·99 ± 0·05 by potentiometric titration, c = 0·0098M) and the spectrum in unbuffered water (the latter is not reproducible). Acid strengths are lower in ethanol,[17] increasing the chance of obtaining the neutral form in unbuffered solvent. In Table 2, data from the literature are compared with spectra in 0·01N-ethanolic sulphuric acid and sodium ethoxide, indicating (although pK_a and pK_b in ethanol are unknown) that the first were essentially spectra of the neutral form.

FIG. 3. *Solvent*: 20N-*sulphuric acid* (except 2-*ethoxypyridene* 1-*oxide in* 10N *acid*).

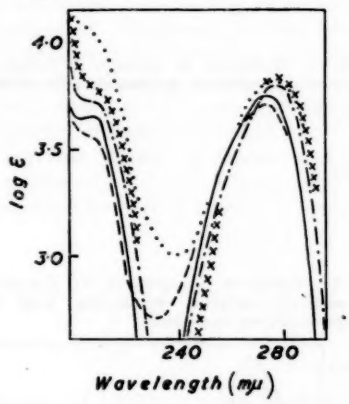
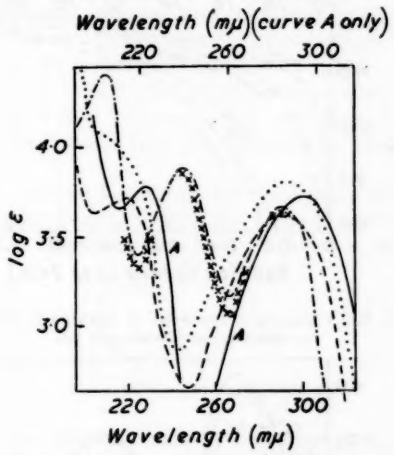


FIG. 4. *Solvent*: *water* (*except* 2-*hydroxypyridine* 1-*oxide in* 0·01N-H_2SO_4).



FIGS. 3 & 4. ———— 2-*Hydroxypyridine* 1-*oxide.* — · — · — 2-*Methoxypyridine* 1-*oxide.*
××××× 2-*Ethoxypyridine* 1-*oxide.* ····· 1-*Benzyloxypyrid*-2-*one.*
— — — — 1-*Methoxypyrid*-2-*one.*

Figs. 3 and 4 give spectra of cationic and neutral 2-hydroxypyridine 1-oxide and alkylated derivatives. Those of the cations are similar (cf. the expected difference in hydrogen-bonding). In 2-aminopyridine 1-oxide, methyl substitution of amino-groups

TABLE 2. *Ultraviolet spectra of* 2-*hydroxypyridine* 1-*oxide in ethanol.*

Solvent	λ_1	ε_1	$\lambda_{infl.}$	ε_i	λ_2	ε_2
EtOH [3]	228	7200	—	—	305	4600
EtOH [3]	228	6500	—	—	305	4000
0·01N-H_2SO_4–EtOH	230	6500	—	—	303	4750
0·01N-NaOEt–EtOH	225	23,200	244	5700	323	6800

causes bathochromic shifts [8] of *ca.* 8 mμ, the bathochromic effect of *C*-alkyl groups (*ca.* 5 mμ) is well known,* and *p*-methoxydiphenyl has $\lambda_{max.}$ 260 compared with 256 for *p*-hydroxydiphenyl.[18] In Fig. 4 the spectrum of 2-hydroxypyridine 1-oxide is displaced by 6 mμ relatively to the alkylated derivatives; it is thus difficult to deduce its structure. However, the spectral effect of *O*-alkylation varies; often no shift or a hypsochromic shift

* However, introduction of methyl groups into the 2-, 3-, or 4-position in pyridine causes shifts of +6·5, +5, and −3·5 mμ respectively [Ikekawa, Maruyama, and Sato, *Pharm. Bull.* (*Japan.*), 1954, **2**, 209].

[15] Koch, *J.*, 1951, 512.
[16] See, *e.g.*, Farmer and Thomson, *Chem. and Ind.*, 1957, 112.
[17] Brown, McDaniel, and Häfliger in Braude and Nachod's "Determination of Organic Structures by Physical Methods," Academic Press, New York, 1955, p. 619 ff.
[18] Burawoy, Cais, Chamberlain, Liversedge, and Thompson, *J.*, 1955, 3727.

is shown, *e.g.*, 3-methoxy- ($\lambda_{max.}$ 223, 262, and 299) and 3-hydroxy-pyridine 1-oxide (224·5, 263·5, 304);[19] this appears to be especially true in chelated phenols.[18] Thus Spring's[3] and Shaw's[2] evidence, while suggestive, is less conclusive than has been accepted (see, *e.g.*, ref. 6).

The changes in the spectra of 2-amino- and 2-hydroxy-pyridine 1-oxide from (dilute) acid to alkaline solution are similar (Fig. 2). It is known that the change in the former compound is loss of a proton from the *N*-oxide-oxygen atom of the cation, to give 2-aminopyridine 1-oxide as such; this perhaps indicates that the proton in 2-hydroxypyridine 1-oxide is more strongly bound to *N*-oxide oxygen.

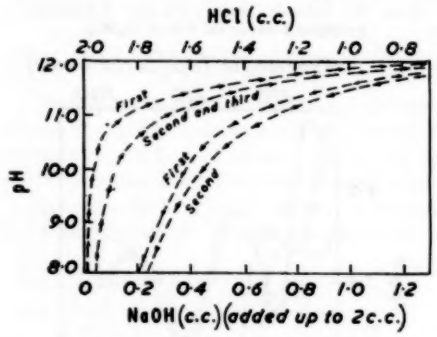
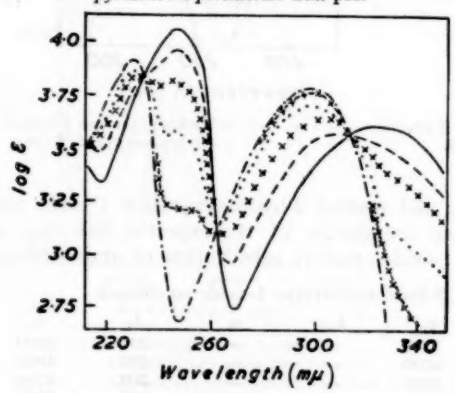


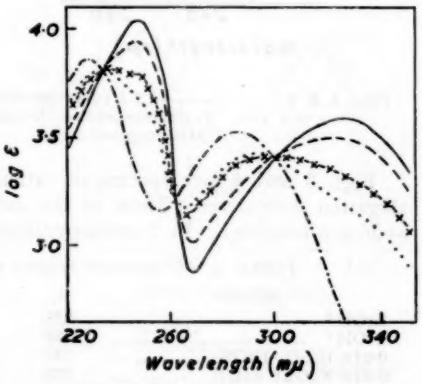
FIG. 5. *Hysteresis in titration of 2-amino-1-methoxypyridinium perchlorate with alkali.*

FIG. 6. *Variation of spectrum of 2-amino-1-methoxypyridinium perchlorate with* pH.



——— 3N- *and* N-, — — — 0·1N-, × × × × 0·03N-, ····· 0·01N-, *and* ×—×—× 0·003N-*Sodium hydroxide.* —·—·— *Water,* 0·01N- *and* 0·1N-*hydrochloric acid.*

FIG. 7. *Variation of spectrum of 2-amino-1-methoxypyridinium perchlorate with time (in* N-*sodium hydroxide).*



——— *After* 8 *min.,* — — — 60 *min.,* ×—×—× 115 *min.,* ····· 180 *min.,* —·—·— 1250 *min.*

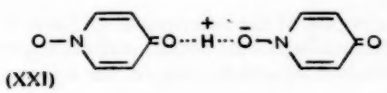
One of us has concluded[8] from ultraviolet spectra comparisons that 2-aminopyridine 1-oxide exists in the amino-form. In the potentiometric titrations, all the 1-methoxypyridinium salts (but not 2-aminopyridine 1-oxide) showed hysteresis (cf., *e.g.*, Fig. 5). It was at first thought that the non-superimposition of the forward- and backward-titration curves for 2-amino-1-methoxypyridinium perchlorate was due to decomposition, which would invalidate the previous[8] conclusions. In a detailed study of the spectrum of this compound in aqueous alkali, it was found to vary with both hydroxyl-ion concentration and time (Figs. 6 and 7). The first product (XVIII or possibly XIX or XX) behaves as a base

[19] Prins, *Rec. Trav. chim.*, 1957, **76**, 58.

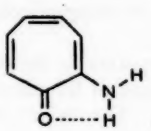
(p*K* 12·4 from Fig. 6), shown to be in equilibrium with starting material; adding acid at once (but not after 48 hr.) to the salt in 0·1N-alkali gave the curve for acid solutions. The slow reaction is possibly decomposition into 2-aminopyridine and formaldehyde, a reaction known for compounds of this type.[20] This reaction did not occur *via* (XVIII) because the rate of appearance of the decomposition product spectrum was similar in N- and 0·1N-alkali (decomposition at the alkali concentration used in the titrations was negligible in the time required for titration). The curve previously given [8] for 2-amino-1-methoxypyridinium perchlorate in 0·1N-sodium hydroxide is misleading, but the true curve for (XVIII) is different from the curves for 2-dimethylamino-, 2-monomethylamino-, and 2-aminopyridine 1-oxide (themselves similar [8]), and this is further evidence for the existence of 2-aminopyridine 1-oxide as such.

The ultraviolet spectrum of 2-aminopyridine 1-oxide does not vary with time or alkali concentration; 1-methoxypyridinium perchlorate shows marked changes, at present under investigation. Hysteresis in the titrations of 2 : 6-dihydroxypteridine with alkali has been explained by " covalent hydration." [21] Ochiai *et al.*[22] record the decomposition of 4-amino-1-methoxy-pyridinium and -quinolinium iodide to pyridine or quinoline and formaldehyde on treatment with silver oxide; Oda [23] states that the quinolinium salt is not easily decomposed by alkalis.

Infrared Spectra.—4-Amino- and 4-hydroxy-pyridine 1-oxide in the solid state have been studied by Costa, Blasina, and Sartori,[7] who concluded that the former could be interpreted on both the imino- or (more probably) the amino-structure. A band at 1648



(XXI)



(XXII)

and none at 1600 was adduced as evidence for the pyridone form in 4-hydroxypyridine 1-oxide but the spectrum was considered best explained by the hydrogen-bridged structure (XXI).

The above work was hindered by the insolubility of the compounds; we have now measured 2-hydroxy- and 2-amino- and 2- and 4-methylamino-pyridine 1-oxide in Nujol mulls and as 0·2M- (0·1 mm. cell) and 0·02M-solutions (1 mm. cell) in chloroform: the results for the 3 mμ region are shown in Table 3.

The spectrum of 4-methylaminopyridine 1-oxide shows strong intermolecular hydrogen-bonds in the solid state, partly broken up in 0·2M- and completely in 0·02M-solution. Both the position and the intensity of the unassociated imino-band agree with the values given by Goulden [24] for 2-methylaminopyridine (3450 cm.$^{-1}$, ε 100), showing that it exists in the methylamino-form.

2-Hydroxypyridine 1-oxide is shown to be strongly intramolecularly hydrogen-bonded, by its spectrum and molecular weight (cryoscopic in benzene, 109). Tropolone (pyridone is related to pyrrole as tropone is to benzene) shows [15] in dilute solution a broad band centred at *ca.* 3100 cm.$^{-1}$; β-diketone enols (containing a six-membered chelate ring) show [25] broad absorption centred at *ca.* 2700 cm.$^{-1}$. Koch concludes [15] from the hydrogen-bond strength (*ca.* 7 kcals./mole) that in tropolone the hydrogen atom is not (instantaneously) symmetrically placed; but is so on a time average (cf. ammonia and the bifluoride ion). The same should hold for 2-hydroxypyridine 1-oxide, but here disymmetry

[20] Katritzky, *Quart. Rev.*, 1956, **10**, 395.
[21] Albert, Lister, and Pedersen, *J.*, 1956, 4621; cf. Brown and Mason, *J.*, 1956, 3443.
[22] Ochiai, Katada, and Naito, *J. Pharm. Soc. Japan*, 1944, **64**, 210; *Chem. Abs.*, 1951, **45**, 5154.
[23] Oda, *J. Pharm. Soc. Japan*, 1944, **64**, 6; *Chem. Abs.*, 1951, **45**, 8523.
[24] Goulden, *J.*, 1952, 2939.
[25] Rasmussen, Tunicliffe, and Brattain, *J. Amer. Chem. Soc.*, 1949, **71**, 1068.

enables one position to be filled on the average more than the other. Taking the evidence as a whole, the compound probably exists mainly as 1-hydroxypyrid-2-one.

2-Aminopyridine 1-oxide is shown to be intermolecularly hydrogen-bonded in the solid, but not in solution (no significant difference on dilution). The two bands of equal

TABLE 3. *Infrared spectra of substituted pyridine 1-oxides in 3 μ region.*

Subst.:	4-NHMe	2-OH	2-NH_2	2-NHMe
Nujol mull	3500—2600 (br) 3250 (sh), 2930	3200—2200 (br) 3070, 2940, 2400	3400—2800 (br) 3250 (sh), 3070 (sh), 2940	(Not measured)
$CHCl_3$ (0·2M) ...	3450 (55), 3240 (75)	3200—2300 (br)	3500 (70) 3360 (70)	3360 (65)
$CHCl_3$ (0·02M)...	3440 (90)	3200—2700 (br)	3480 (55) 3340 (50)	3360 (65)

(ε_A is given for solution spectra). br = broad region of absorption. sh = shoulder.

intensity at *ca.* 3490 and 3350 cm.$^{-1}$ indicate that it exists in the amino-form. Goulden,[24] and Angyal and Werner,[26] have shown that non-associated amino-pyridines, etc., absorb at *ca.* 3500 and 3400 cm.$^{-1}$ in solution.

2-Methylaminopyridine 1-oxide absorbs at 3360 cm.$^{-1}$, and the lowering of the frequency relatively to that of the (unassociated) 4-isomer shows that it is intramolecularly hydrogen-bonded.

The infrared spectrum of 2-aminotropone has been discussed by Japanese workers,[27] who record bands at 2·83 and 2·97 μ (3540 and 3370 cm.$^{-1}$), and consider that a weak hydrogen-bond was formed (XXII). Short [28] has shown that 1-aminoacridine (3494, 3390 cm.$^{-1}$) and 8-aminoquinoline (3493, 3389 cm.$^{-1}$) are intramolecularly hydrogen-bonded.

The infrared spectra in the 6—12·5 μ region of the compounds in Table 3 have been compared with those of the alkylated derivatives of both forms, and other pyridines and pyridine 1-oxides. The results, to be published separately, support the above conclusions.

TABLE 4. *Parts of amino- or hydroxy-form present per part of imino- or pyridone form.*

	4-Amino-	2-Amino-	4-Hydroxy-	2-Hydroxy-
Pyridine 1-oxide	$>10^7$	$>10^8$	*ca.* 1	(see text)
Pyridine	2×10^3 [a]	2×10^6 [a]	4×10^{-4} [b]	3×10^{-3} [b]

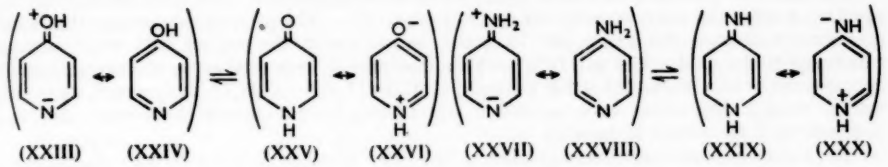
[a] Ref. 10. [b] Ref. 11.

Discussion.—Table 4 shows the proportions of the tautomers of 2- and 4-amino- and -hydroxy-pyridine and 1-oxides at equilibrium in solution as determined by basicity measurements. The usual explanation for the predominant existence of 4-hydroxypyridine in the pyridone form, but of, *e.g.*, 4-aminopyridine in the amino-form, is that in the tautomerism between the hydroxy- (XXIV) and pyridone form (XXV) account has to be taken of mesomerism with, respectively, (XXIII) and (XXVI). As negative charge is more stable on oxygen the equilibrium is swung in favour of the pyridone form. But in tautomerism of the aminopyridine (XXVIII) and 4-pyridone imine (XXIX), the form (XXX) is not much more stable than (XXVII) and the amino-form is favoured because of greater benzenoid resonance.

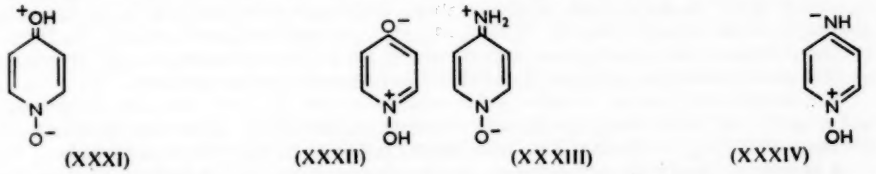
The influence of the oxygen atom in the corresponding pyridine 1-oxides can now be considered. The canonical form (XXXI) would be expected to be relatively more favoured than (XXIII), but (XXXII) less so than (XXVI); thus the equilibrium in the hydroxy-compounds should be less in favour of the pyridone form. In the amino-compounds, because (XXXIII) is relatively more favoured than (XXVII), and (XXXIV) less so than

[26] Angyal and Werner, *J.*, 1952, 2911.
[27] Nozoe, Seto, Takeda, Morosawa, and Matsumoto, *Proc. Japan. Acad.*, 1951, **27**, 556; *Chem. Abs.*, 1952, **46**, 7559; Kuratani, Tsuboi, and Shimanouchi, *Bull. Chem. Soc., Japan*, 1952, **25**, 250; *Chem. Abs.*, 1953, **47**, 8516.
[28] Short, *J.*, 1952, 4584.

(XXX), the equilibrium would be expected to be still more in favour of the amino-form than in the pyridine series. Table 4 shows that this is so.

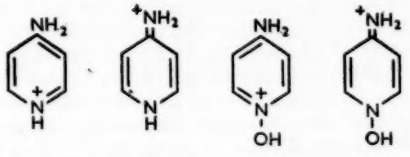


(XXIII) (XXIV) (XXV) (XXVI) (XXVII) (XXVIII) (XXIX) (XXX)



(XXXI) (XXXII) (XXXIII) (XXXIV)

The most important canonical forms of protonated 4-aminopyridine are (XXXV) and (XXXVI), those of protonated 4-aminopyridine 1-oxide are (XXXVII) and (XXXVIII), and it would be expected that the introduction of an *N*-oxygen atom would considerably lower the stability of a protonated aminopyridine. As this introduction of an oxygen atom



(XXXV) (XXXVI) (XXXVII) (XXXVIII)

lowers the stability of the pyridone imine form of an aminopyridine, but raises that of the amino-form, it should follow that (i) the intrinsic basicity of a hydroxy- or amino-pyridine 1-oxide (in the hydroxy- or amino-form) is much lower than that of the deoxygenated analogue, (ii) the difference between the basicities of a 1-hydroxypyridone or its imine and their deoxygenated analogues should be much less, and in either direction. Reference to the last column of Table 1 shows that all these predictions are borne out, except that 2-methoxypyridine 1-oxide is more strongly basic than expected, presumably because of hydrogen-bonding in (XIII).

Experimental

4-Aminopyridine 1-Oxide.—4-Nitropyridine 1-oxide (70 g.) was stirred under hydrogen with 2% palladium–strontium carbonate (14 g.) in ethanol (500 c.c.) at *ca.* 60°, until uptake of hydrogen (15—20 l./hr.) almost ceased. Evaporation and crystallisation of the residue from ethanol–ethyl acetate gave the amino-oxide (43 g., 78%) obtained on recrystallisation in tablets, m. p. 235—236° (lit.,[12] m. p. 229°) (Found: C, 54·6; H, 5·6. Calc. for $C_5H_6ON_2$: C, 54·6; H, 5·5%). Light absorption: max. at 270 mμ (ε 15,500) in 0·1N-hydrochloric acid; 276 mμ (ε 18,900) in 0·1N-sodium hydroxide.

The picrate (needles from ethanol) had m. p. 203—204° (lit.,[12] 201·5—202°,[13] 199—200°) (Found: C, 39·2; H, 2·9. Calc. for $C_{11}H_9O_8N_5$: C, 38·9; H, 2·7%); the *picrolonate* (beige laths from ethanol) had m. p. 241—244° (decomp.) (Found: C, 48·2; H, 3·9. $C_{15}H_{14}O_6N_6$ requires C, 48·2; H, 3·8%).

4-Amino-1-methoxypyridinium Salts.—The above amine, heated with one equivalent of methyl toluene-*p*-sulphonate for 12 hr. at 100°, gave the *toluene*-p-*sulphonate* (84%), deliquescent plates (from ethanol–ethyl acetate), m. p. 127—129° (Found: C, 53·0; H, 5·3. $C_{13}H_{16}O_4N_2S$ requires C. 52·7; H, 5·4%). This salt (0·6 g.) in ethanol (1·2 c.c.) and perchloric acid (0·32 c.c.) gave the *perchlorate* (36%) (plates from ethanol–ethyl acetate) m. p. 99—101°

(Found: C, 32·3; H, 4·1. $C_6H_9O_5N_3Cl$ requires C, 32·1; H, 4·0%). Light absorption: max. at 274 mμ (ε 19,300) in 0·1N-hydrochloric acid; 273 mμ (ε 19,900) in 0·1N-sodium hydroxide.

4-*Methylaminopyridine* 1-*Oxide*.—25% Aqueous methylamine (139 c.c.) and 4-chloropyridine 1-oxide (23·1 g.) were heated for 20 hr. at 140°. The product was evaporated with potassium carbonate (23 g.) at 100°/15 mm.; extraction of the residue with ethyl methyl ketone gave the *oxide* (17·4 g., 78%), which crystallised from the same solvent in highly deliquescent prisms, m. p. 192—194° (Found: C, 57·7; H, 6·6. $C_6H_8ON_2$ requires C, 58·0; H, 6·5%). Light absorption: max. at 279 mμ (ε 16,400) in 0·1N-hydrochloric acid; 285 mμ (ε 22,800) in 0·1N-sodium hydroxide.

The *picrate* (prisms from ethanol) had m. p. 193—194° (Found: C, 41·0; H, 3·3. $C_{12}H_{11}O_8N_5$ requires C, 40·8; H, 3·1%); the *picrolonate* (beige needles from ethanol) had m. p. 211—212° (decomp.) (Found: C, 49·9; H, 4·1; N, 21·1. $C_{16}H_{16}O_6N_6$ requires C, 49·5; H, 4·1; N, 21·6%).

The product of heating this amine with methyl toluene-*p*-sulphonate did not crystallise; no solid perchlorate or tetrachloroferrate [29] could be prepared from this product.

4-*Dimethylaminopyridine* 1-*Oxide*.—After sublimation at 160°/0·05 mm., this compound [30] had m. p. 97—99° with resolidification and remelting at 214—216°. Light absorption max. at 288 mμ (ε 19,200) in 0·1N-hydrochloric acid, 289 mμ (ε 23,800) in 0·1N-sodium hydroxide.

4-*Dimethylamino*-1-*methoxypyridinium Salts*.—Prepared as the 4-amino-analogues, the *toluene*-p-*sulphonate*, deliquescent prisms (from ethanol–ethyl acetate) had m. p. 109—112° (Found: C, 55·4; H, 6·4. $C_{15}H_{20}O_4N_2S$ requires C, 55·6; H, 6·2%); the *perchlorate* (81%) (needles from ethanol) had m. p. 138—139° (Found: C, 38·1; H, 5·3; N, 10·8. $C_8H_{13}O_5N_2Cl$ requires C, 38·0; H, 5·2; N, 11·1%). Light absorption: max. at 290 mμ (ε 23,500) in 0·1N-hydrochloric acid; 291 mμ (ε 20,900) in 0·1N-sodium hydroxide.

1-*Methoxypyrid*-4-*one*.—4-Hydroxypyridine 1-oxide (2·22 g.), ethanolic sodium ethoxide (from 200 c.c. of ethanol and 0·46 g. of sodium), and methyl toluene-*p*-sulphonate (3·92 g.) were refluxed for 1 hr. (pH then 7). The cooled (solid carbon dioxide and ethanol) mixture was filtered and evaporated at 100°/20 mm. (during which two further filtrations were necessary). Extraction of the residue with chloroform (2 × 15 c.c.) and distillation of the extracts gave the *pyridone* (1·7 g., 68%), b. p. 190—195° (bath)/0·1 mm., highly deliquescent prisms, m. p. 60—65° after sublimation at 100°/0·1 mm. (Found: C, 57·6; H, 5·7. $C_6H_7O_2N$ requires C, 57·6; H, 5·6%). Light absorption: max. at 243 mμ (ε 11,200) in 5N-sulphuric acid; 262 mμ (ε 16,800) in water (Ochiai *et al.*[1,31] records b. p. 160°/0·01 mm. and states that it crystallised in a desiccator but that m. p. determination was difficult.)

The picrate (from ethanol) had m. p. 200—202° (lit.,[1] m. p. 200—201°).

1-*Benzyloxypyrid*-2-*one*.—2-Chloropyridine 1-oxide (20·9 g.) and charcoal (1 g.) were refluxed for 5 min. with sodium benzyloxide in benzyl alcohol (200 c.c. containing 3·72 g. of sodium), and the solution was filtered and concentrated at 140°/20 mm. Extraction with ethyl acetate (180 c.c.) (with 1 g. of charcoal), removal of solvent at 100°/20 mm., and recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) gave the pyridone (18·1 g., 56%), sufficiently pure for reduction. Sublimation at 120°/0·1 mm. and further recrystallisation raised the m. p. to 76—78°; the product was identical (mixed m. p. and infrared spectrum) with a sample (m. p. 77—79°) prepared by Shaw's method [2] (Found: C, 71·8; H, 5·3; N, 6·75. Calc. for $C_{12}H_{11}O_2N$: C, 71·6; H, 5·5; N, 7·0%) (lit.,[2] m. p. 85—86°). Light absorption max. at 297 mμ (ε 6200), infl. at 214 mμ (ε 11,400) in water; max. at 279 mμ (ε 6400), infl. at 207 mμ (ε 11,600) in 20N-sulphuric acid.

In our hands attempted preparation [2] of 2-benzyloxypyridine 1-oxide by perbenzoic acid oxidation of 2-benzyloxypyridine gave mainly 1-benzyloxypyrid-2-one (ultraviolet spectra).

2-*Hydroxypyridine* 1-*Oxide*.—The above pyridone (15 g.) in ethanol (60 c.c.), shaken over 5% palladium–charcoal (0·75 g.), absorbed 1700 c.c. of hydrogen (at 1 atm.) in 85 min. Filtration hot, and evaporation, gave the oxide (6·85 g., 83%), m. p. 148—149° after recrystallisation from ethyl acetate–light petroleum (b. p. 40—60°) (Found: C, 54·2; H, 4·5; N, 12·6. Calc. for $C_5H_5O_2N$: C, 54·1; H, 4·5; N, 12·6%) (lit.,[2] m. p. 149—150°). Light absorption: max. at 209, 276 mμ (ε 4300, 5600) in 20N-sulphuric acid; 225, 296 mμ (ε 6400, 5200) in 0·001N-sulphuric acid; 210, 313 mμ (ε 26,700, 6200), infl. at 237 mμ (ε 6200) in 0·1N-sodium hydroxide.

[29] Blatt and Gross, *J. Amer. Chem. Soc.*, 1955, **77**, 5424.
[30] Katritzky, Randall, and Sutton, *J.*, 1957, 1769.
[31] Ochiai, Teshigawara, Oda, and Naito, *J. Pharm. Soc. Japan*, 1945, **65**, 516A, 1; *Chem. Abs.*, 1951, **45**, 8527.

2-Ethoxypyridine 1-Oxide.—2-Chloropyridine 1-oxide (2·6 g.) was refluxed for 30 min. with ethanolic sodium ethoxide (20 c.c. containing 0·46 g. of sodium) (pH then 7—8). Evaporation at 100°/20 mm., extraction with chloroform (2 × 15 c.c.), removal of solvent, and recrystallisation from ethanol–ethyl acetate gave the oxide (2·24 g., 80%), m. p. (after further recrystallisation) 71—73° (softens from 67°) (lit.,[32] m. p. 71—73°). Light absorption: max. at 280 mμ (ε 7000) infl. at 209 mμ (ε 6200) in 10N-sulphuric acid; max. at 214, 249, 293 mμ (ε 27,200, 7400, 4500) in water. The picrate had m. p. 110—111° (lit.,[32] m. p. 111—113°).

2-Methoxypyridine 1-Oxide.—Prepared as the last compound, the *oxide* (68%) formed hygroscopic needles, m. p. 78—79°, from ethyl acetate (Found: C, 57·8; H, 5·7. $C_6H_7O_2N$ requires C, 57·6; H, 5·6%). Light absorption: max. at 280 mμ (ε 6300), infl. at 210 mμ (ε 5200) in 20N-sulphuric acid; max. at 213, 249, 293 mμ (ε 25,000, 7600, 4500) in water.

It formed a *hydrate* in air, as prisms, m. p. 66·5—67·5° (Found: C, 48·0; H, 6·7; N, 8·9. $C_6H_7O_2N,1{\cdot}5H_2O$ requires C, 47·4; H, 6·6; N, 9·2%). The *picrate* (needles from ethanol) had m. p. 140—143° (Found: C, 41·0; H, 2·8; N, 15·6. $C_{12}H_{10}O_9N_4$ requires C, 40·7; H, 2·8; N, 15·8%).

1-Methoxypyrid-2-one.—Prepared as for the 4-analogue the *pyrid-2-one* (77%) had b. p. 130° (bath)/0·05 mm.; it partially solidified (Found: C, 57·8; H, 5·9. $C_6H_7O_2N$ requires C, 57·6; H, 5·6%). Light absorption: max. at 276 mμ (ε 5200), infl. at 207 mμ (ε 3800) in 20N-sulphuric acid; max. at 224, 296 mμ (ε 5300, 4100) in water. This compound did not readily form a picrate in ethanol.

4-Methoxypyridine 1-Oxide.[13]—Light absorption: max. at 244 mμ (ε 12,000) in 5N-sulphuric acid; 261 mμ (ε 16,300) in water.

This investigation was carried out during the tenure (by A. R. K.) of an I.C.I. Fellowship. Some analyses are by Mr. F. C. Hall, M.A. The spectra were obtained by Mr. F. Hastings and Mrs. W. Sheldon under the supervision of Dr. F. B. Strauss, using a Cary recording spectrophotometer (model 14M-50) and a Perkin-Elmer recording infrared spectrophotometer (model 21).

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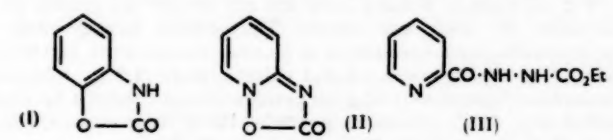
[32] Newbold and Spring, *J.*, 1948, 1864.

NOTES.

876. N-*Oxides and Related Compounds. Part VI.** *Some Derivatives of 2-Aminopyridine 1-Oxide.*

By A. R. KATRITZKY.

PREPARATIONAL details (cf. ref. 1) are given for 2-aminopyridine 1-oxide hydrochlorides required for other work. As benzoxazolone (I) has antifungal properties,[2] derivatives of



the isoelectronic pyridino-oxadiazolone (II)[3] were made, but later the parent compound was found inactive. Whereas *iso*nicotinoyl hydrazide with carbonyl chloride gives

* Part V, Gardner and Katritzky, preceding paper.

[1] Katritzky, *J.*, 1957, 191.
[2] Virtanen and Hietala, *Acta Chem. Scand.*, 1955, **9**, 1543.
[3] Katritzky, *J.*, 1956, 2063.

2-4′-pyridyl-1-oxa-3 : 4-diazol-5-one,[4] *N*-ethoxycarbonyl-*N*′-picolinoylhydrazine (III) is pyrolysed to *NN*′-dipicolinoylhydrazine.

Experimental.—*2-Ethoxycarbonylaminopyridines.* Ethyl chloroformate (14 c.c.) was added gradually to 2-amino-5-methylpyridine (13·5 g.) in pyridine (60 c.c.) with cooling. After 12 hr., water was added; the resulting *2-ethoxycarbonylamino-5-methylpyridine* (14·9 g., 67%) formed needles (from ethanol), m. p. 144·5—145·5° (Found: C, 60·1; H, 6·7; N, 15·3. $C_9H_{12}O_2N_2$ requires C, 60·0; H, 6·7; N, 15·5%). Similarly prepared were *2-ethoxycarbonylamino-4 : 6-dimethylpyridine* (84%), prisms, m. p. 62—64°, from aqueous ethanol (Found: C, 62·0; H, 7·3. $C_{10}H_{14}O_2N_2$ requires C, 61·9; H, 7·2%); 2 : 6-di(ethoxycarbonylamino)pyridine (32%), prisms, m. p. 132—133°, from ethanol (lit.,[5] m. p. 127°) (Found: C, 52·5; H, 6·0; N, 16·7. Calc. for $C_{11}H_{15}O_4N_3$: C, 52·2; H, 5·9; N, 16·6%); and *2-ethoxycarbonylaminoquinoline* (65%), needles, m. p. 98—100°, from ethanol (Found: C, 66·7; H, 5·6; N, 12·8. $C_{12}H_{12}O_2N_2$ requires C, 66·7; H, 5·6; N, 13·0%).

2-Aminopyridine 1-oxide hydrochlorides. 2-Ethoxycarbonylamino-5-methylpyridine (14·9 g.), acetic acid (32 c.c.), and 30% hydrogen peroxide (13 c.c.) were heated 18 hr. at 70°, then evaporated at 100°/15 mm., and the residue was refluxed for 18 hr. with concentrated hydrochloric acid (20 c.c.). Evaporation and recrystallisation from ethanol gave *2-amino-5-methylpyridine 1-oxide hydrochloride* (6·0 g. 45%), prisms, m. p. 195—198° (Found: C, 45·0; H, 5·8; N, 17·1. $C_6H_9ON_2Cl$ requires C, 44·9; H, 5·6; N, 17·4%). The following were similarly prepared: *2-amino-4 : 6-dimethyl-* (65%), needles, m. p. 230—231° (decomp.) from ethanol (Found: C, 48·6; H, 6·4. $C_7H_{11}ON_2Cl$ requires C, 48·2; H, 6·3%), and *2-amino-6-methyl-pyridine 1-oxide hydrochloride* (67%), prisms (from ethanol), m. p. 212—214° (Found: C, 45·0; H, 5·7; N, 16·9%); *2-aminoquinoline 1-oxide hydrochloride* (56%), needles from ethanol, m. p. 255—257° (decomp.) (Found: C, 55·2; H, 4·7. $C_9H_9ON_2Cl$ requires C, 55·0; H, 4·6%).

2-Ethoxycarbonylaminopyridine 1-oxides. The 2-ethoxycarbonylaminopyridines were oxidised with peracetic acid as described [3] to give: *2-ethoxycarbonylamino-5-methyl-* (83%), prisms, m. p. 90—93° (from ethyl acetate) (Found: N, 14·3. $C_9H_{12}O_3N_2$ requires N, 14·3%), *2-ethoxycarbonylamino-4 : 6-dimethyl-* (86%), needles, m. p. 111—112° (from ethyl acetate) (Found: C, 57·3; H, 6·7; N, 13·1. $C_{10}H_{14}O_3N_2$ requires C, 57·2; H, 6·7; N, 13·3%), and 2 : 6-*di*(*ethoxycarbonylamino*)*pyridine 1-oxide* (74%), prisms, m. p. 114—116° (from ethyl acetate) (Found: C, 49·5; H, 5·7; N, 15·2. $C_{11}H_{15}O_5N_3$ requires C, 49·1; H, 5·6; N, 15·6%); and *2-ethoxycarbonylaminoquinoline 1-oxide* (91%) plates, m. p. 102—104° (from ethyl acetate) (Found: C, 61·8; H, 5·2; N, 12·2. $C_{12}H_{12}O_3N_2$ requires C, 62·1; H, 5·2; N, 12·1%).

From the oxidation of crude 2-ethoxycarbonylamino-5-methylpyridine a by-product (cf. ref. 3) was obtained: NN′-*di*-(*5-methyl-2-pyridyl*)*urea* 1 : 1′-*dioxide* (7%), m. p. 248—250° [decomp.], from acetic acid (Found: C, 56·8; H, 5·4. $C_{13}H_{14}O_3N_4$ requires C, 56·9; H, 5·1%).

Pyridino-oxadiazolones. Heating the above urethane oxides (cf. ref. 3) gave: *5′-methylpyridino-*, needles, m. p. 197—198° (from ethanol) (Found: C, 56·4; H, 4·2; N, 18·4. $C_7H_6O_2N_2$ requires C, 56·0; H, 4·0; N, 18·7%), *4′ : 6′-dimethylpyridino-*, needles, m. p. 167—168° (from ethanol) (Found: C, 58·7; H, 4·9; N, 16·7. $C_8H_8O_2N_2$ requires C, 58·6; H, 4·9; N, 17·0%), and *quinolino*-(1′ : 2′-2 : 3)-1-*oxa*-2 : 4-*diazol*-5-*one*, needles, m. p. 176—177° (from ethanol) (Found: C, 64·6; H, 3·4; N, 15·7. $C_{10}H_6O_2N_2$ requires C, 64·5; H, 3·2; N, 15·1%).

Pyridino-(1′ : 2′-2 : 3)-1-oxa-2 : 4-diazol-5-one did not inhibit the growth of *Microsporum gypseum, M. audonini, M. canis* var. *album, Trichophyton mentagrophytes, T. rubrum, T. sulphureum,* or *Helminthosporium monoceras* in glucose peptone broth in 0·008M-solution.

N-Ethoxycarbonyl-N′-picolylhydrazine. Ethyl chloroformate (1·2 g., 1·05 c.c.) was added during 10 min. to picolinoylhydrazine (1·37 g.) in pyridine (3 c.c.). After 4 hr. water was added, to give the *product* (1·32 g., 72%), prisms, m. p. 126·5—127·5° (from ethanol) (Found: C, 52·1; H, 5·3; N, 19·7. $C_9H_{11}O_3N_3$ requires C, 51·7; H, 5·3; N, 20·1%).

NN′-Dipicolylhydrazine. (*a*) The above hydrazine (2 g.) was heated from 230° to 300° in 15 min., and kept at 300° for 10 min. The residue, crystallised from pentyl alcohol, gave NN′-*dipicolylhydrazine* (0·6 g., 52%), prisms, m. p. 220—223° (from ethanol) (Found: C, 59·6; H, 4·3; N, 23·4. $C_{12}H_{10}O_2N_4$ requires C, 59·5; H, 4·1; N, 23·1%).

[4] Smith, *Science*, 1954, **119**, 514.
[5] Meyer and Malley, *Monatsh.*, 1892, **23**, 407.

(*b*) Potassium nitrite (0·25 g.) in water (2 c.c.) was slowly added to picolinylhydrazine (0·68 g.) in acetic acid (2 c.c.) and ice (10 g.). After 10 min., 30% aqueous potassium carbonate (2 c.c.) was added; after a further 30 min. the base (0·34 g. 56%) was collected; it had m. p. 223—224·5° (from ethanol) (Found: C, 59·8; H, 4·4%) and was identical with the above specimen (infrared spectra and mixed m. p.).

We thank Mrs. K. Crawford of the Sir William Dunn School of Pathology, Oxford, for the biological measurements. This work was done during the tenure of an I.C.I. Research Fellowship.

THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, May 23rd*, 1957.]

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877. *The Preparation of Hydronium Forms of Analcite and Chabazite by Ion-exchange.*

By I. R. BEATTIE and A. DYER.

TREATMENT of aluminosilicates with mineral acids usually results in formation of an amorphous solid. However, Barrer *et al.*[1] have found that treatment of the silver form of certain aluminosilicates with a solution of a halide, where the cation is too large to enter the crystals, results in the precipitation of silver halide together with an increase in the pH of the solution. In order to examine this type of reaction further it was decided to treat silver forms of analcite and chabazite with pyridinium chloride solutions, whereby the pH of the solution would be maintained approximately constant in the event of hydrogen-ion exchange.

Experimental.—Silver forms of analcite and chabazite were prepared as described previously.[2] Hydrochloric acid was partially neutralised with pyridine to a pH value of between 5 and 6. Silver chabazite (about 1 g.) was heated under reflux with the pyridine–hydrochloric acid solution (50 ml.) for 1 day. The solid was then filtered off and extracted with pyridine until no further change in weight occurred. In this way all the silver chloride formed during the reaction was removed. The product was examined for hydrogen-ion activity by treatment with aqueous sodium hydroxide. The solid was analysed for residual silver, examined by *X*-ray powder photography, and studied under the microscope. Water content was determined by direct ignition.

With silver analcite the treatment was similar except that the exchange was carried out in a sealed tube at 120°. This process was then repeated after an initial extraction with pyridine had shown limited exchange to have occurred.

During ignition of the exchanged forms it was noted that, contrary to the usual formation of a glassy solid, the residue was a fine powder. Further, although the initial silver forms of the zeolite were discoloured to some extent (presumably by silver or silver oxide) the final product was white. The results of these experiments (Table) indicate that although the removal of

Reactant	*X*-Ray examn. of product	Water (wt.-%)	Exchange (mole-%)	H available (atom-%)
Silver analcite	Typical analcite spacings	17·1	~ 90	~10
Silver chabazite	Typical chabazite spacings	26·4	~100	~80

silver is almost quantitative in both cases, it is probable that with the analcite considerable quantities of amorphous material are formed. This was borne out by the difficulty experienced in obtaining a good *X*-ray powder photograph, long exposures being essential. The small amount of exchange with sodium hydroxide solution is not unexpected, since a silicate, of the formula $(H_2O)_2O,Al_2O_3,4SiO_2,xH_2O$ when amorphous, is to be regarded as $Al_2O_3,4SiO_2,yH_2O$,

[1] Barrer and Raitt, *J.*, 1954, 4641; Barrer and Sammon, *J.*, 1955, 2838; 1956, 675.
[2] Beattie, *Trans. Faraday Soc.*, 1954, **50**, 581.

showing no evidence of hydrogen ions. Apparently the very stable chabazite structure is much less affected by this exchange. In view of the presence of amorphous material, water-content measurements must be treated with caution.

Discussion.—Silicate glasses undergo very rapid exchange with hydrogen ions in water,[3,4] yielding a strongly alkaline solution. With zeolites, such as analcite, the equivalent reaction does not occur, despite the great facility with which these minerals undergo ion exchange. The difference in behaviour is probably due to presence of terminal oxygens in the glass. A hydrogen or hydronium ion adjacent to an Si–O grouping will presumably, by covalent linking, become Si–O–H. The activity of hydrogen ions within the silicate may then be extremely small, so that the equilibrium for the exchange would lie on the side of a hydrogen glass. In this way hydrogen-ion exchange could occur even in alkaline solution. In the zeolites now studied there are no terminal oxygen atoms, the structures being a three-dimensional array of aluminium and silicon tetrahedrally surrounded by four oxygen atoms, with each oxygen linked to either two silicon or a silicon and an aluminium atom. Examination of the behaviour in neutral solution of silicates containing a terminal oxygen atom could be of value in considering the structure of glass. The amount of hydrogen-ion exchange might then be indicative of the presence of singly-linked oxygen atoms.

It is well known that aluminium does, in fact, enhance the resistance of many glasses to corrosion. It has also been shown [4] that the diffusion coefficient for sodium-ion migration is lowered if, for a given glass composition, silicon is partially replaced by aluminium. For every aluminium atom so introduced there would be one less terminal oxygen atom. However, the calculation of the diffusion coefficient assumes the equilibrium position to be that of a hydrogen glass, the concentration of sodium ions at time infinity being zero. An erroneous infinity value (due to only partial hydrogen-ion exchange) would lead to an incorrect diffusion coefficient, since this is found from the relation

$$Q = 2A(C - C_\infty)[(Dt)/\pi]^{\frac{1}{2}}$$

where Q = quantity of material which has diffused across the plane $x = 0$ up to time t; D = diffusion coefficient; C = concentration of diffusing material initially; C_∞ = concentration of diffusing material at time infinity; and A = surface area of the solid.

KING'S COLLEGE, STRAND, LONDON, W.C.2. [*Received, February 22nd,* 1957.]

[3] Douglas and Isard, *J. Soc. Glass Tech.*, 1949, **33**, 289.
[4] Beattie, *Trans. Faraday Soc.*, 1953, **49**, 1059.

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878. *The Formation of Peroxymonosulphuric Acid and Peroxydisulphuric Acid in Solutions of Sulphuric Acid Irradiated by* ^{60}Co *Radiation.*

By M. DANIELS, J. LYON, and J. WEISS.

SUGGESTIONS that during the radiolysis of aqueous sulphate [1] or sulphuric acid solution [2] the solutes can participate in free-radical reactions have recently received indirect support.[3] However, direct evidence has hitherto been absent; recent results with pure sulphuric acid solutions [4] can only be interpreted as a consequence of direct absorption of energy by the sulphuric acid.

[1] Allen, Hochanadel, Ghormley, and Davis, *J. Phys. Chem.*, 1952, **56**, 575.
[2] Allen, *Radiation Res.*, 1954, **1**, 85.
[3] Sworski, *J. Amer. Chem. Soc.*, 1956, **78**, 1768.
[4] Hochanadel, Ghormley, and Sworski, *ibid.*, 1955, **77**, 3215.

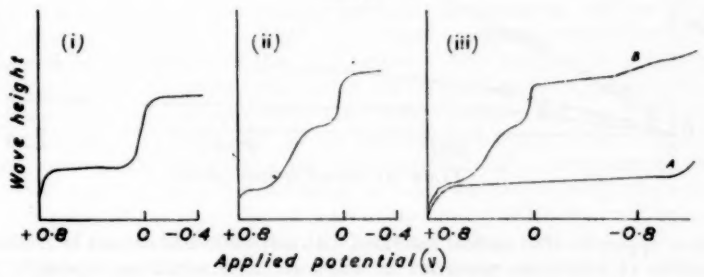
The present work demonstrates the existence of peroxymonosulphuric acid and peroxydisulphuric acid in solutions of sulphuric acid, irradiated in presence of air; their formation provides clear evidence of radical attack on the sulphuric acid molecule or its anions.

Analysis of mixtures of small amounts of peroxymono- and peroxydi-sulphuric acid in presence of hydrogen peroxide—which is always formed in irradiated, aerated aqueous solutions—is complicated by interrelation by hydrolysis and mutual interference by induced reactions.[5,6] Several independent methods have therefore been used.

In the polarogram hydrogen peroxide gives a well-defined, broad wave at $-1{\cdot}3$ to $-0{\cdot}5$ v (against the standard calomel electrode)[7] and peroxydisulphuric acid a sharp wave at $+0{\cdot}1$ v).[8,9] Caro's acid has not been investigated previously, but it should give a wave at a still more positive potential.

Polarograms were obtained by the usual methods, a Cambridge pen-recording instrument being used. Fig. 1 shows the results for (i) a solution of peroxydisulphuric acid (4×10^{-4}M), (ii) a similar solution after partial hydrolysis, and (iii) an un-irradiated and an irradiated 2·5M-solution of sulphuric acid. In the last, the peroxydisulphate wave can be

FIG. 1.



(i), *Potassium peroxydisulphate* (4×10^{-4}M). (ii), *Solution* (i) *after hydrolysis.* (iii), 2·5M-*Sulphuric acid*: (*A*), *unirradiated*; (*B*), *irradiated.*

readily identified; there is also a broader wave at a half-wave potential of $+0{\cdot}4$ v and this is also found in hydrolysed solutions of peroxydisulphate. If the second wave is accepted as being due to Caro's acid, *viz.*, $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$, this would indicate the presence of this compound in irradiated solutions of sulphuric acid. Hydrogen peroxide can be identified and estimated separately by the specific titanium sulphate reagent.[10] Csanyi and Solymosi's method[11] is suitable for other micro-estimations; this involves addition of arsenite to the acid solution to remove the Caro's acid; the hydrogen peroxide can then be estimated cerimetrically and excess of arsenite back-titrated with ceric salt, with osmium tetroxide as catalyst. Finally, the peroxydisulphuric acid is hydrolysed with hot sulphuric acid in the presence of arsenite, and the consumption of the latter is again estimated by ceric titration. By a combination of these methods, hydrogen peroxide and peroxymono- and peroxydi-sulphuric acid have been determined in solutions of sulphuric acid irradiated (^{60}Co) in presence of air. Some typical results are shown in Fig. 2. In 0·4M-sulphuric acid the yields of the per-acids are relatively low, but still significant,

[5] Gleu, *Z. analyt. Chem.*, 1931, **195**, 61.
[6] Berry, *Analyst*, 1933, **58**, 464.
[7] Kolthoff and Lingane, "Polarography," Interscience Publ., Inc., New York, 1952.
[8] Kolthoff, Guss, May, and Medalia, *J. Polymer Sci.*, 1946, **1**, 340.
[9] Bernard, *Compt. rend.*, 1933, **236**, 2412.
[10] Eisenberg, *Ind. Eng. Chem. Anal.*, 1943, **15**, 327.
[11] Csanyi and Solymosi, *Z. analyt. Chem.*, 1954, **142**, 423.

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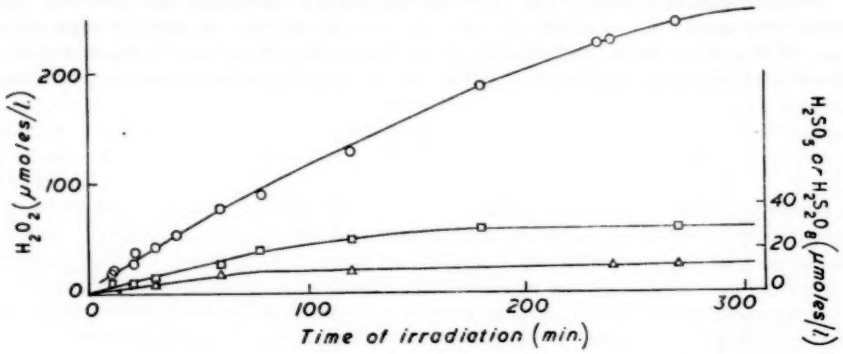
e.g., at a dose of $2{\cdot}4 \times 10^{-5}$ mole ev/ml. there were found 5·6 μmoles/l. of peroxymono-acid, 3·2 μmoles/l. of peroxydi-acid, and 316 μmoles/l. of hydrogen peroxide. The yields of the products are generally in the sequence: $H_2O_2 > H_2SO_5 > H_2S_2O_8$, the absolute values being dependent on the concentration of sulphuric acid. The yields of both peroxy-mono- and peroxydi-sulphuric acid, though not that of hydrogen peroxide, appear to reach a stationary state after a certain dose of radiation.

The mere presence of peroxydisulphuric acid seems a strong indication of the intermediate formation of HSO_4 radicals, with subsequent dimerisation.

FIG. 2. *Irradiation of* 2M*-solutions of sulphuric acid with* ^{60}Co *γ-rays. Yields of products as functions of dose: dose rate,* 1×10^{-7} *mole* ev/*ml./min.* ⊙ H_2O_2 □ H_2SO_5 △ $H_2S_2O_8$.



It is now apparent, that radical reactions with sulphuric acid cannot be neglected in the interpretation of radiolytic processes in sulphuric acid solutions, especially when the reactions of the radical so produced (*e.g.* HSO_4) are different from those of its precursor (OH). It cannot yet be definitely concluded whether the sulphuric acid molecule is concerned in this reaction, *viz.* $OH + H_2SO_4 \longrightarrow H_2O + HSO_4$, or the bisulphate ion, $OH + HSO_4^- \longrightarrow OH^- + HSO_4$, although there is some evidence, that the sulphate ion can probably be excluded.

Work is in progress to elucidate the behaviour of dilute and concentrated solutions of sulphuric acid and the rôle of oxygen in these systems.

Thanks are due to King's College for the award of the Levine Studentship (J. L.), to Pilkington Bros. (J. L.), and to the Director of the Atomic Energy Research Establishment, Harwell, for support and for permission to publish this Communication.

KING'S COLLEGE, NEWCASTLE UPON TYNE, 1. [*Received, April* 23*rd,* 1957.]

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879. *The Reactions of Gaseous Fluorine and Chlorine with Liquid* n*-Butane and* iso*Butane.*

By P. C. ANSON and J. M. TEDDER.

n-BUTANE and *iso*butane have been fluorinated and chlorinated by bubbling a mixture of the gaseous halogen and nitrogen through the liquid hydrocarbon illuminated by visible light. The reactions were carried out at four temperatures and the products estimated by gas-phase chromatography. The results are summarised in the Table. The relative

rates of substitution of the different hydrogen atoms are thus in the expected order, tertiary > secondary > primary for both reactions, but fluorination is considerably less selective than chlorination. Chlorination becomes less selective as the temperature is raised but fluorination appears to be unaffected. We believe that the apparent insensitivity of this fluorination to changes in temperature is due to the reaction's occurring at quite high temperature in the gas phase of the bubbles. As a bubble forms at the inlet some butane will evaporate into it (vapour pressure [1] of butane at −60° is 43 mm.) and then react almost instantaneously. The heat of reaction will warm the bubble and thereby increase the rate of evaporation of the hydrocarbon. This butane will in turn react and raise the temperature of the bubble still further (the latent heat of vaporisation [2] of butane is 5·3 kcal./mole compared with approximately 100 kcal./mole for the heat of the reaction [3]). It is possible, therefore, that the bulk of the reaction may occur in the vapour phase at temperatures very much higher than the surrounding liquid. In agreement with this, the distribution of the products in fluorination at −80° was considerably affected by slight changes in the sinter at the inlet, *i.e.*, changes in the site at which the bubbles are formed had a greater effect on the reaction than a 70° change in temperature.

The proportions of primary to secondary or tertiary halide obtained by reaction of liquid butane and iso*butane with mixtures of gaseous nitrogen and fluorine or chlorine.*

[The extent of halogenation was about 15% for fluorine and about 7% for chlorine. The composition of gaseous mixture was F_2 (or Cl_2) : N_2 = 1 : 4. Figures in parentheses are the number of runs at each temperature.]

Hydrocarbon	Temp.	Proportion in product: fluorn.	chlorn.	Hydrocarbon	Temp.	Proportion in product: fluorn.	chlorn.
n-Butane	−101°	1·34 (1)	0·28 (1)	*n*-Butane	−33°	1·32 (2)	0·48 (1)
,, ...	− 80	1·21 (9)	0·32 (3)	*iso*Butane	−80	4·01 (3)	0·92 (2)
,, ...	− 67	1·18 (2)	0·39 (1)	,, ...	−33	—	2·28 (1)

The chlorination probably also occurs partly in the gas phase, but the heat of reaction is much less (*ca.* 25 kcal./mole), and some of the reaction may occur in the liquid. This belief is supported by some chlorinations in solvent. A dilute solution of chlorine in tetrachloroethane was added to a dilute solution of butane in the same solvent. The solution was irradiated for half an hour at −35° ± 5° before being analysed. The distribution of monochlorides (primary : secondary = 0·53) was not greatly different from that obtained with gaseous chlorine. An attempt to apply the same procedure to fluorine was thwarted by the insolubility of fluorine in either tetrachloroethane or carbon tetrachloride.

The present work failed to give results for a really quantitative comparison of fluorination and chlorination, but it is the first precise study of aliphatic mono-fluorination. Attention has now been turned to gas-phase reactions.

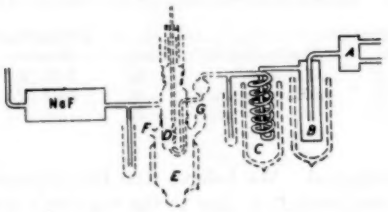
Apparatus (*see Figure*).—Fluorine (from a generator) or chlorine (from a cylinder) was mixed with a metered flow of " oxygen free " nitrogen in vessel *A* and then passed through trap *B* (at −80°) and coil *C* in which the gas was cooled to the reaction temperature. In " Pyrex " reaction vessel *D* the inlet tube ended in a coarse sinter. Vessel *D* fitted into a second glass vessel *E*, the lower half of which formed a silvered Dewar flask. A low-boiling solvent [ethylene, b. p. −101°; " Arcton 3 " (CF_3Cl), b. p. −81°; hydrogen bromide, b. p. −67°; ammonia, b. p. −33°) was condensed into *E* through inlet *F*, and its level in *E* kept above the level of the hydrocarbon inside vessel *D*. The outside of *E* was illuminated by two 100-watt lamps.

The products from fluorinations were poured into a cold vessel containing anhydrous sodium fluoride and samples were taken directly from this vessel for injection into the gas-phase

[1] Wackher, Linn, and Grosse, *Ind. Eng. Chem.*, 1945, **37**, 464.
[2] Aston and Messerly, *J. Amer. Chem. Soc.*, 1940, **62**, 1917.
[3] Tedder, *Chemistry and Industry*, 1955, 508.

chromatography column. Products of chlorinations were left in the reaction vessel for ½ hr. after the supply of chlorine had been stopped, while the nitrogen stream continued and entrained out any unchanged chlorine and the hydrogen chloride formed.

Gas-phase Chromatography.—A conventional chromatography column, of 9 mm. " Pyrex " tubing, was packed with Celite 545 and dinonyl phthalate, according to James and Martin's method.[4] The effective length was 7 ft. The fractions were detected after elution by the change in thermal conductivity of the gas stream as measured by the usual katharometer device. The whole column and the katharometers were maintained at a constant temperature



Thick lines represent copper; broken lines glass.

according to the products being analysed. The carrier gas was " oxygen free " nitrogen flowing at 30 c.c./min. The products were identified by comparing their elution times with synthetic mixtures of authentic fluoro- and chloro-butanes. By studying synthetic mixtures it was confirmed that the areas under the peaks of the chromatogram were proportional to the weight of isomers injected. No products formed by fission of carbon bonds were detected, and the total yield of polyhalogenated compounds was less than 0·1% under the conditions described. Small amounts of butenes may have been formed but these could not be separated from the large excess of unchanged butane. An average of five chromatograms was obtained for each halogenation.

The authors thank Imperial Chemical Industries (General Chemicals Division) for the loan of a fluorine generator and for supplies of " Arcton 3," the British Petroleum Company for a gift of *n*-butane, and the Director of the Chemical Research Laboratory, Teddington, for assistance in supplying *n*-butane and *iso*butane. One of them (P. C. A.) is indebted to the D.S.I.R. for a maintenance grant.

THE UNIVERSITY, SHEFFIELD. [*Received, May 13th,* 1957.]

[4] James and Martin, *Biochem. J.*, 1952, **50**, 679.

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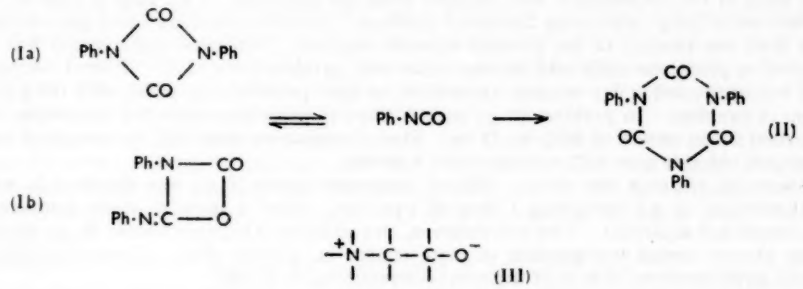
880. *The Polymerisation of Aromatic* iso*Cyanates.*

By J. IDRIS JONES and N. G. SAVILL.

THE chemistry of *iso*cyanates was recently reviewed by Arnold, Nelson, and Verbanc.[1] Catalysts such as pyridine, methylpyridines, triethylamine, *N*-methylmorpholine,[2] and triethylphosphine and other alkyl- or dialkylaryl-phosphines induce dimerisation of phenyl *iso*cyanate. The symmetrical structure (Ia) was originally assigned to the dimer, but an alternative (Ib) has been postulated and some support presented. Crystallographic and infrared studies support structure (Ia), but it is possible that a catalysed rearrangement occurs in solution. When heated with a small amount of potassium acetate phenyl *iso*cyanate gives the trimer (II); sodium benzoate in dimethylformamide is also a useful catalyst for the trimerisation.[3]

[1] Arnold, Nelson, and Verbanc, *Chem. Rev.*, 1957, **57**, 47; *J. Chem. Educ.*, 1957, **34**, 158.
[2] Kogon, *J. Amer. Chem. Soc.*, 1956, **78**, 4911.
[3] Balon, Barthel, Kehr, Langerak, Pelley, Simons, Smeltz, and Stallmann, Abs. Papers, 130th Meeting, Amer. Chem. Soc. Atlantic City, N.J. Sept. 1956, p. 15P.

In an attempt to prepare *N*-substituted oxazolid-2-ones by condensation of epoxides with aromatic *iso*cyanates, a trace of pyridine being used as catalyst, it was discovered that trimerisation of the *iso*cyanate occurred exclusively under these conditions. Thus, phenyl *iso*cyanate in solution in ethylene oxide, propylene oxide, styrene oxide, or epichlorohydrin with a trace of pyridine gave high yields of triphenyl *iso*cyanurate (II)



when kept; no reaction occurred in absence of pyridine. Tertiary bases open the epoxide ring [4] and the catalytic action in this case is believed to be due to the initial formation of structure (III). Cetylpyridinium chloride also had some catalytic activity, a 48% yield of trimer being obtained in 1 month with 2% of this catalyst. Whilst the dimerisation is reversible [2] the trimerisation is irreversible, and when phenyl *iso*cyanate dimer was dissolved in epichlorohydrin containing a catalytic amount of pyridine, the product was triphenyl *iso*cyanurate.

The behaviour of diphenylyl and 1- and 2-naphthyl *iso*cyanates has also been studied. With epichlorohydrin and a small amount of pyridine, and careful exclusion of moisture, some trimerisation always occurred. The m. p.s reported by Raiford and Freyermuth [5] for the corresponding dimers obtained by polymerisation with triethylphosphine [270° (decomp.), ~296° (sublimes), and 196—197°, compared with 374°, 335°, and 344°] support the trimeric structures, as do the infrared absorption spectra. Kogon [2] observed that triphenyl *iso*cyanurate and other tri-(*ortho*-substituted aryl) *iso*cyanurates have one carbonyl absorption band at 1703—1694 cm.$^{-1}$. We find that triphenyl *iso*cyanurate gives a single absorption band at 1711 cm.$^{-1}$; the other three products give single peaks in the same region (see Table). The spectrum of dimeric phenyl *iso*cyanate, on the other hand, exhibits a twin carbonyl absorption band at 1773 and 1756 cm.$^{-1}$. In contrast to the spectra of tri-(*para*-substituted aryl) *iso*cyanurates [2]—three main absorption peaks in the range 1766—1680 cm.$^{-1}$—that of trisdiphenylyl *iso*cyanurate had a single band at 1709 cm.$^{-1}$.

Trimer of	M. p.	C=O band (cm.$^{-1}$)	Found (%), C	H	N	Requires (%), C	H	N
Phenyl *iso*cyanate	285°	1711	70·3	4·2	11·8	70·6	4·2	11·8
Diphenylyl *iso*cyanate	374	1709	79·8	4·8	7·1	80·0	4·7	7·2
1-Naphthyl ,, ...	335	1713	77·8	4·3	7·9	78·1	4·2	8·3
2-Naphthyl ,, ...	344	1700	77·7	4·0	8·3	78·1	4·2	8·3

The dimeric and trimeric forms of 2 : 4-di*iso*cyanatotoluene have been prepared.[1,3,6,7] We have found that in propylene oxide or epichlorohydrin, with pyridine as catalyst, this di*iso*cyanate is converted into a resin. Presumably, some of the *ortho* as well as the *para*

[4] Bradley, Forrest, and Stephenson, *J.*, 1951, 1592.
[5] Raiford and Freyermuth, *J. Org. Chem.*, 1943, **8**, 230.
[6] Saunders and Hardy, *J. Amer. Chem. Soc.*, 1953, **75**, 5439.
[7] Seifken, *Annalen*, 1949, **562**, 75.

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*iso*cyanate groups have been involved in the polymerisation, the resin appearing to be highly cross-linked.

Experimental.—Trimerisation of phenyl iso*cyanate.* Phenyl *iso*cyanate (10 g.) in epichlorohydrin (8 g.) with 1 drop of pyridine was kept at room temperature for 2 days. The crystalline product (10 g.) obtained was triphenyl *iso*cyanurate, m. p. 285° (lit. 282°). Similarly a quantitative yield of the *iso*cyanurate was obtained from the *iso*cyanate (5 g.) after 3 days at 0° in ethylene oxide (10 g.) containing 2 drops of pyridine. In both cases there was slight contamination from the product of the pyridine–epoxide reaction. Extensive trimerisation was also observed in propylene oxide and styrene oxide with pyridine as catalyst. Phenyl *iso*cyanate (5 g.) was unaffected in dry benzene, chloroform, or light petroleum (b. p. 60—80°) (10 g.) with 1 drop of pyridine. In pyridine (5 g.) with 2 drops of propylene oxide the *iso*cyanate (5 g.) trimerised to the extent of 92% in 24 hr. Phenyl *iso*cyanate with 2% by weight of cetylpyridinium chloride gave 48% of trimer after 1 month.

Conversion of dimer into trimer. Phenyl *iso*cyanate dimer (1 g.) was dissolved in warm epichlorohydrin (5 g.) containing 1 drop of pyridine. After 5 days at room temperature some trimer had separated. This was removed, and addition of light petroleum (b. p. 60—80°) to the filtrate caused precipitation of more trimer, m. p. 273—274°. Chromatography on alumina gave altogether 0·85 g. of triphenyl *iso*cyanurate, m. p. 282°.

Polymerisation of diphenylyl and 1- *and* 2-*naphthyl* iso*cyanates.* The *iso*cyanate (5 g.) from a sealed ampoule was dissolved in epichlorohydrin (10 g.) to which was added 2 drops of pyridine. With diphenylyl *iso*cyanate extensive deposition of crystals occurred during 24 hr.; with 1- and 2-naphthyl *iso*cyanate only after 1 month was there appreciable crystallisation. Despite precautions to exclude moisture, some water was picked up during the working up, which involved addition of light petroleum (b. p. 60—80°) followed by extraction of the precipitated solids with hot acetone. It was subsequently found that the starting materials had also been exposed to moisture before being sealed. The presence of ureas complicated separation of the trimers. Thus, some *sym*-bisdiphenylyl-, -di-1-naphthyl-, and -di-2-naphthyl-ureas, m. p.s 321°, 298°, and 310°, were recovered, dimethylformamide proving a useful solvent for crystallisation. From the acetone-soluble portions the trimeric *iso*cyanates were isolated in low yields (> 22%).

Polymerisation of 2 : 4-*di*iso*cyanatotoluene.* A firm gel was obtained when the di*iso*cyanate (4·8 g.) was set aside for 24 hr. in propylene oxide (10 ml.) containing 1 drop of pyridine. On removal of the solvent at 100° *in vacuo* a completely insoluble resin was obtained. 2 : 4-Di-*iso*cyanatotoluene (7 g.) in epichlorohydrin (10 ml.) containing 1 drop of pyridine gave a similar insoluble polymer during 24 hr. at room temperature.

Infrared absorption spectra. The compounds were examined as mulls in Nujol, a modified Hilger D 209 double-beam instrument being used.

This work is published by permission of the Director of the Laboratory. The authors are indebted to Mr. W. Kynaston for the infrared absorption data.

CHEMICAL RESEARCH LABORATORY, TEDDINGTON, MIDDLESEX. [*Received, May 16th,* 1957.]

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881. *Some* α- *and* β-DL-*Aspartyl Peptides.*

By Y. LIWSCHITZ and A. ZILKHA.

PEPTIDES composed of two amino-acids, each of which contains an asymmetric carbon atom, should exist in two racemic forms. The fact that in only relatively few instances were both actually isolated may be due either to the preferential formation of one racemic form under the conditions of the reaction, or to the formation of mixed crystals.[1] We have now isolated the two stereoisomeric racemates of β-DL-aspartyl-DL-α-aminobutyric acid and of β-DL-aspartyl-DL-valine, and of their ethyl esters and *N*-benzyl derivatives.

Synthesis of ethyl (*N*-benzyl-α-DL-aspartyl)-DL-α-aminobutyrate from the mixed

[1] Fischer, "Untersuchungen ueber Aminosaeuren, Polypeptide und Proteine (1899—1906)," Julius Springer, Berlin, 1906, p. 42.

anhydride of *N*-benzyl-DL-aspartic acid and chloroformic acid [2] gave a 30% yield of material of m. p. 86°, together with an isomeric compound (A), m. p. 186° in, 15% yield. The latter differed from ethyl (*N*-benzyl-β-DL-aspartyl)-DL-α-amino-*n*-butyrate (B) prepared by the maleic anhydride method,[3] and so must be a second modification of either the α- or the β-isomer. This was confirmed as follows.

Both the free dipeptide ester and the dipeptide derived from substance (A) gave a negative biuret reaction and a blue spot with ninhydrin on paper chromatograms, in contradistinction to the α-isomer which gave a positive biuret reaction and a purple spot. α-Isomers of all known ethyl esters of (*N*-benzyl-DL-aspartyl)-dipeptides melt at least 50° below the corresponding β-derivatives and are more soluble in water and ethanol. Thus in accordance with previous findings,[2,4] substance (A) belongs to the β-series.

Coupling DL-valine ethyl ester with the same mixed anhydride of *N*-benzyl-DL-aspartic acid yielded the *N*-benzyl-dipeptide ester (B) (13%; m. p. 170°) (no α-derivative could be isolated) which represented a second racemic modification of the β-isomer according to the above criteria; the substance (A) obtained in our previous work [3] melted at 179—181°.

It has been shown [5-7] that the infrared spectra of optically " pure " (LL, DD) dipeptides differ markedly from those of the " mixed " (LD, DL) diastereoisomers, especially in the appearance of strong additional bands in the spectra of the latter. On this basis it seems that the higher-melting isomers, designated (A), are of the " mixed " type. Strong bands in the spectrum of ethyl (*N*-benzyl-β-aspartyl)-α-aminobutyrate (A) but not in that of the (B) compound occur at 3·0, 3·3, 6·6, and 7·6 μ. In ethyl (*N*-benzyl-α-aspartyl)-α-aminobutyrate, the C=O stretching band appears at 5·95 and not at 6·0 μ, as for all β-derivatives. Strong bands present in the spectrum of (*N*-benzyl-β-aspartyl)valine ethyl ester (A), but not in that of the (B) isomer, appear at 3·3 and 7·4 μ.

β-Alanine ethyl ester coupled to yield almost exclusively the (*N*-benzyl-α-DL-aspartyl)-β-alanine ester from which the free dipeptide was prepared in the usual manner.

Use of a 4-molar excess of the amino-ester in the coupling reaction resulted in preferential formation of α-dipeptides. Thus (*N*-benzyl-α-DL-aspartyl)-DL-alanine ethyl ester was formed with the use of an excess of DL-alanine ester, but not when merely equivalent amounts were used.

Efforts to obtain the free α-DL-aspartyl-DL-alanine were unsuccessful, and on hydrogenolysis of (*N*-benzyl-α-DL-aspartyl)-DL-alanine (which could not be isolated from the mixture after hydrolysis of the ester) the peptide bond was completely disrupted and only the two component amino-acids were detected on paper-chromatograms. That the peptide bond was still intact after the hydrolysis was unequivocally proved by the absence of a positive ninhydrin-reacting substance.

Experimental—M. p.s were determined in a Fisher–Johns apparatus and the ascending method of paper partition chromatography was used (80% phenol). Infrared absorption spectra were examined in potassium bromide discs with a Baird double-beam instrument.

Ethyl (*N-benzyl*-β-DL-*aspartyl*)-DL-α-*aminobutyrate* (*A*) *and ethyl* (*N-benzyl*-α-DL-*aspartyl*)-DL-α-*aminobutyrate*. To a cooled solution of the mixed anhydride of *N*-benzyl-DL-aspartic and chloroformic acid [2] (from 4·4 g. of *N*-benzyl-DL-aspartic acid) were added triethylamine (2 g.) and then ethyl DL-α-aminobutyrate (2·6 g.). After the mixture had been kept overnight at room temperature, triethylamine hydrochloride was filtered off and the solution evaporated *in vacuo* to dryness. The residue was dissolved in acetone (30 ml.) and left at 0° for 4 days. There separated *ethyl* (*N-benzyl*-β-DL-*aspartyl*)-DL-α-*aminobutyrate* (*A*) (1 g., 15%), m. p. 181°,

[2] Liwschitz and Zilkha, *J. Amer. Chem. Soc.*, 1954, **76**, 3698.
[3] *Idem, ibid.*, 1955, **77**, 1265.
[4] LeQuesne and Young, *J.*, 1952, 24.
[5] Otey and Greenstein, *Arch. Biochem. Biophys.*, 1954, **53**, 501.
[6] Ellenbogen, *J. Amer. Chem. Soc.*, 1956, **78**, 369.
[7] Blackburn and Tetley, *Biochim. Biophys. Acta*, 1956, **20**, 423.

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raised to 186° on recrystallization from ethanol or water (Found: C, 60·6; H, 7·1; N, 8·2. $C_{17}H_{24}O_5N_2$ requires C, 60·6; H, 7·1; N, 8·3%).

To the filtrate was added dry ether until the appearance of cloudiness. Storage at 0° for 1 week gave the *N*-benzyl-α-dipeptide ester, m. p. 80° (2 g., 30%). After two recrystallizations from water it melted at 86°. It gave a positive bluish biuret reaction (Found: C, 60·2; H, 7·0; N, 8·3%).

Ethyl α-DL-*aspartyl*-DL-α-*aminobutyrate*. This *compound*, obtained in almost quantitative yield by hydrogenolysis of the preceding compound,[2] had m. p. 187° (from water–acetone) and gave positive ninhydrin and biuret reactions [Found: N, 11·1; N (Van Slyke), 5·6. $C_{10}H_{18}O_5N_2$ requires N, 11·4; N (Van Slyke), 5·7%].

α-DL-*Aspartyl*-DL-α-*aminobutyric acid*. Ethyl (*N*-benzyl-α-DL-aspartyl)-DL-α-aminobutyrate (1·6 g.) was left in N-lithium hydroxide (14 ml.) for 90 min. at room temperature. The solution was then acidified with hydrochloric acid and evaporated to dryness *in vacuo*. The residue was dissolved in glacial acetic acid (50 ml.) and hydrogenated with 0·3 g. of catalyst. Filtration, evaporation *in vacuo*, dissolution of the residue in hot absolute ethanol, re-evaporation, and recrystallization from water–acetone yielded the free *dipeptide*, m. p. 202° (0·45 g., 43%), giving a bluish biuret reaction and a purple spot on paper chromatograms (R_P 0·31) [Found: C, 43·5; H, 6·4; N, 12·5; N (Van Slyke), 6·3. $C_8H_{14}O_5N_2$ requires C, 44·0; H, 6·4; N, 12·8; N (Van Slyke), 6·4%].

Ethyl β-DL-*aspartyl*-DL-α-*aminobutyrate* (*A*). Hydrogenolysis as for the corresponding α-derivative gave an almost quantitative yield of this ester as *monohydrate* (from aqueous ethanol), m. p. 114°, giving a negative biuret and a positive ninhydrin test [Found : N, 10·6; N (Van Slyke), 5·4. $C_{10}H_{18}O_5N_2,H_2O$ requires N, 10·6; N (Van Slyke), 5·3%].

β-DL-*Aspartyl*-DL-α-*aminobutyric acid* (*A*). Ethyl (*N*-benzyl-β-DL-aspartyl)-DL-α-aminobutyrate (A) (0·5 g.) was left in N-sodium hydroxide (5 ml.) for 2 hr. at room temperature. After acidification with hydrochloric acid the solution was evaporated to dryness. The residue was taken up in glacial acetic acid (20 ml.) and catalyst (0·2 g.) added. Hydrogenolysis was carried out for 6 hr. The recovered *dipeptide* had m. p. 208° (0·12 g., 30%), with a negative biuret reaction and giving a bluish spot on paper chromatograms (R_F 0·39) [Found: C, 43·0; H, 6·3; N, 12·4; N (Van Slyke), 6·3%)].

(*N*-*Benzyl*-β-DL-*aspartyl*)-DL-*valine ethyl ester* (B). To a cooled solution of the mixed anhydride from 4·4 g. of *N*-benzyl-DL-aspartic acid was added DL-valine ethyl ester (5·8 g.). Treatment was then continued as in the coupling with ethyl DL-α-aminobutyrate but the mixture was left at 0° for 2 weeks, giving an *ester* (0·9 g., 13%), m. p. 170° (from ethanol) (Found: C, 61·8; H, 7·4; N, 7·9. $C_{18}H_{26}O_5N_2$ requires C, 61·6; H, 7·4; N, 8·0%).

β-DL-*Aspartyl*-DL-*valine ethyl ester* (*B*), obtained in almost quantitative yield by hydrogenolysis, had m. p. 118° (from ethanol–ether) and gave a positive ninhydrin but a negative biuret reaction [Found: C, 47·3; H, 7·7; N, 10·2; N (Van Slyke), 5·1. $C_{11}H_{20}O_5N_2,H_2O$ requires C, 47·2; H, 7·9; N, 10·0; N (Van Slyke), 5·0%].

β-DL-*Aspartyl*-DL-*valine* (*B*). The *N*-benzyl-dipeptide ester (0·8 g.) was left in N-lithium hydroxide (7 ml.) for 2 hr. at room temperature, acidified with hydrochloric acid, and evaporated *in vacuo*. Further treatment and isolation as above gave the acid (0·2 g., 38%), m. p. 224° (from water–acetone) [negative biuret reaction and a blue spot on paper chromatograms (R_F 0·43)] [Found: C, 45·8; H, 6·9; N, 11·7; N (Van Slyke), 6·0. Calc. for $C_9H_{16}O_5N_2$: C, 46·5; H, 6·9; N, 12·1; N (Van Slyke), 6·0%].

(*N*-*Benzyl*-α-DL-*aspartyl*)-β-*alanine ethyl ester*. To a cooled solution of the mixed anhydride prepared from 11·2 g. of *N*-benzyl-DL-aspartic acid was added β-alanine ethyl ester (11·7 g.). After 2 days at 0°, some (*N*-benzyl-β-DL-aspartyl)-β-alanine ethyl ester (1·1 g., 7%; m. p. 197°), identified by mixed m. p., was removed and the filtrate evaporated *in vacuo*. The residue was taken up in hot acetone (50 ml.) and left at 0° for 2 days. The ester which crystallized was filtered off and washed with acetone; it (10 g., 63%) had m. p. 132°. Recrystallization from ethanol raised the m. p. to 140°. The *ester* gave a positive biuret reaction (Found: C, 59·8; H, 6·8; N, 8·8. $C_{16}H_{22}O_5N_2$ requires C, 59·6; H, 6·8; N, 8·7%).

β-DL-*Aspartyl*-β-*alanine ethyl ester*, obtained in almost quantitative yield by hydrogenolysis of the preceding compound, had m. p. 188° (from ethanol), and gave positive ninhydrin and biuret reactions (Found: C, 46·9; H, 6·8; N, 12·0. $C_9H_{16}O_5N_2$ requires C, 46·5; H, 6·9; N, 11·9%).

α-DL-*Aspartyl*-β-*alanine*. (*N*-Benzyl-α-DL-aspartyl)-β-alanine ethyl ester (3 g.) was left in

N-sodium hydroxide (21 ml.) for 1 hr. at room temperature. After acidification with hydrochloric acid, the *dipeptide* was obtained in the usual manner (0·5 g., 26%), having m. p. 196° (from water–acetone). It gave a positive biuret reaction and a purple spot on paper chromatograms (R_F 0·36) [Found: C, 41·1; H, 6·1; N, 13·6; N (Van Slyke), 6·9. $C_7H_{12}O_5N_2$ requires C, 41·1; H, 5·9; N, 13·7; N (Van Slyke), 6·9%].

(*N-Benzyl-α-*DL*-aspartyl*)-DL-*alanine ethyl ester*. To a cooled solution of the mixed anhydride from 6·6 g. (0·03 mole) of *N*-benzyl-DL-aspartic acid, was added DL-alanine ethyl ester (14 g., 0·12 mole). The mixture was left for 48 hr. at room temperature and then evaporated *in vacuo*. The residue was taken up in acetone (40 ml.) and left at 0° for 4 days. The crystals were filtered off (1·6 g.; m. p. 140°). Dry ether was added to the filtrate until cloudiness and the whole left at 0° for several more days. The resulting, still somewhat sticky precipitate was washed with acetone and filtered off. An additional 1·1 g. were obtained (total yield of both fractions 28%). On recrystallization from ethanol the m. p. was raised to 144°. In contrast to the β-isomer this *ester* gave a bluish biuret reaction and reacted negatively to copper carbonate (Found: C, 59·6; H, 6·9; N, 8·8. $C_{16}H_{22}O_5N_2$ requires C, 59·6; H, 6·8; N, 8·7%).

α-DL-*Aspartyl-*DL-*alanine ethyl ester*, obtained in almost quantitative yield by hydrogenolysis of the preceding compound, had m. p. 188° (from water–acetone) and gave positive biuret and ninhydrin reactions [Found: C, 45·7; H, 6·8; N, 11·8; N (Van Slyke), 6·1. $C_9H_{16}O_5N_2$ requires C, 46·5; H, 6·9; N, 11·9; N (Van Slyke), 6·0%].

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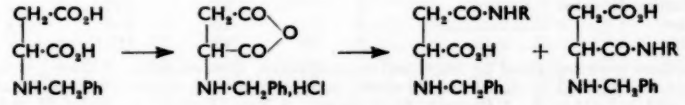
882. *Preparation of Aspartyl Amides and Peptides* via N-*Benzyl-*DL-*aspartic Anhydride Hydrochloride.*

By A. ZILKHA and Y. LIWSCHITZ.

AN additional method for the preparation of aspartyl amides and peptides is based on the use of *N*-benzyl-DL-aspartic anhydride hydrochloride. Treatment of *N*-benzyl-DL-aspartic acid with acetic anhydride causes acetylation of the secondary amino-group in addition to the ring closure,[1] but using cold acetyl chloride–acetic acid (1 : 1) affords *N*-benzyl-DL-aspartic anhydride hydrochloride in 80% yield. If the proportion of acetyl chloride to acetic acid is 3 : 1, the product is *N*-benzyl-DL-aspartic acid hydrochloride, whose identity was proved by comparison with a sample prepared by evaporation *in vacuo* of a solution of *N*-benzyl-DL-aspartic acid in hydrochloric acid.



Reaction of this anhydride with amines and free amino-acid esters in water or acetone gave mainly β-derivatives, accompanied, in some cases, by the α-isomer. The preferential formation of β-amides and peptides when bulky groups are involved is probably due to steric effects, since in the reaction with ammonia, only α-asparagine was isolated.

Reaction with ethyl DL-α-aminobutyrate in acetone afforded two racemic modifications of the β-peptide in addition to the α-isomer.[2] In this and similar instances the isomers were separated by fractional crystallization from ethanol.

Known substances [3-5] were identified by mixed m. p.s and the nature of the linkage in

[1] Liwschitz, Zilkha, and Amiel, *J. Amer. Chem. Soc.*, 1956, **78**, 3067.
[2] Liwschitz and Zilkha, preceding note.

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new amides or peptides was determined by the biuret reaction,[6] reaction with copper carbonate,[7] and the colour with ninhydrin on paper chromatograms.[8]

Experimental.—M. p.s were determined in a Fisher–Johns apparatus.

N-Benzyl-DL-aspartic anhydride hydrochloride. *N*-Benzyl-DL-aspartic acid (11·2 g.) was dissolved in acetyl chloride (40 ml.) and acetic acid (40 ml.) and left overnight at room temperature. The salt which crystallized was filtered off and washed with a little acetic acid and ether: it (8·6 g., 80%) had m. p. 157°; it must be protected from moisture and should always be used freshly prepared (Found: N, 5·5; Cl, 14·6. $C_{11}H_{12}O_3NCl$ requires N, 5·8; Cl, 14·7%).

N-Benzyl-DL-aspartic acid hydrochloride. (*a*) *N*-Benzyl-DL-aspartic acid (11·2 g.) was dissolved in acetyl chloride (60 ml.) and acetic acid (20 ml.). Precipitation began almost at once. After 1 hr. at room temperature, the *salt* was filtered off and washed with ether; it (13 g.) had m. p. 87° (Found: N, 5·1; Cl, 13·5. $C_{11}H_{14}O_4NCl$ requires N, 5·4; Cl, 13·5%). (*b*) *N*-Benzyl-DL-aspartic acid (1 g.) was dissolved in concentrated hydrochloric acid and the solution evaporated *in vacuo*. The hydrochloride was obtained quantitatively with m. p. 87°.

Reactions of alkylamines or amino-esters with *N*-benzyl-DL-aspartic anhydride hydrochloride were carried out according to one of three procedures for each of which one typical example is given, the remainder being summarized in the Table. That with ethyl DL-α-aminobutyrate, which involves the separation of three isomers, is described in full.

(a) *N²-Benzyl-N¹-ethyl-DL-asparagine.* The anhydride (1·2 g.) and ethylamine (0·5 g.) in acetone (10 ml.) were heated under reflux for 30 min., then left at room temperature overnight. The precipitate, recrystallized from ethanol, had m. p. 208° (0·4 g., 32%).

(b) *N-Benzyl-DL-α-asparagine.* The anhydride (1·5 g.) was dissolved in 25% aqueous ammonia (10 ml.) at 0° and the solution was evaporated on the water-bath. The residue was freed from ammonium chloride by trituration with cold methanol, then having m. p. 196° (1 g., 71%). The m. p. was erroneously reported as 180° in a previous communication.[6]

(c) *(N-Benzyl-β-DL-aspartyl)glycine ethyl ester.* The anhydride (2·4 g.) was added to a solution of glycine ethyl ester (2·06 g.) in acetone (15 ml.). Crystallisation started after about 15 min., but the mixture was left at room temperature overnight. The product, washed with acetone and recrystallized from a small quantity of ethanol, had m. p. 201° (1·8 g., 59%).

Preparation of N²-benzyl-DL-aspartyl amides and peptide esters.

(Recrystallized from ethanol, if not indicated otherwise.)

Anhydride treated with	Type of deriv.	Yield (%)	M. p.	Method
Ethylamine	β	48	208°	*b*
Allylamine	β	60	211	*a*
*cyclo*Hexylamine	α [a]	17	189	*a*
	β [a]	33	245 [b]	
Benzylamine	β	74	215 [c]	*b*
p-Toluidine	α [a]	16	184 [d]	*a*
	β [a]	70	224 [e]	
α-Naphthylamine	β	35	199 [c]	*a*
DL-α-Alanine Et ester	β	53	197	*c*
β-Alanine ,,	β	50	195	*c*
DL-Valine ,,	β	40 [c]	170 [f]	*c*

[a] The isomers were separated by fractional crystallization from ethanol. [b] Owing to insolubility the substance was purified by dissolution in alkali, precipitation with hydrochloric acid, and washing with water and hot ethanol. [c] Recryst. from water. [d] New (Found: C, 69·0; H, 6·5; N, 8·9. $C_{18}H_{20}O_3N_2$ requires C, 69·2; H, 6·4; N, 8·9%). Hydrogenolysis yielded *N-tolyl-DL-α-asparagine*, m. p. 235° (from water) (Found: C, 59·2; H, 6·3; N, 12·2. $C_{11}H_{14}O_3N_2$ requires C, 59·4; H, 6·3; N, 12·6%). [e] The mixture was kept at 0° for 2 weeks. [f] Recryst. from a very small volume of ethanol.

Ethyl (N-benzyl-α- and -β-DL-aspartyl)-DL-α-aminobutyrate. The anhydride (2·4 g.) was added to a solution of ethyl DL-α-aminobutyrate (2·6 g.) in acetone (20 ml.) and left at room

[3] Liwschitz, Edlitz-Pfeffermann, and Lapidoth, *J. Amer. Chem. Soc.*, 1956, **78**, 3069.
[4] Frankel, Liwschitz, and Amiel, *ibid.*, 1953, **75**, 330.
[5] Liwschitz and Zilkha, *ibid.*, 1955, **77**, 1265.
[6] *Idem, ibid.*, 1954, **76**, 3698.
[7] Desnuelle and Bonjour, *Biochim. Biophys. Acta*, 1952, **9**, 356.
[8] LeQuesne and Young, *J.*, 1952, 24.

temperature overnight. After cooling in an ice-bath, the precipitate consisting of a mixture of two stereoisomeric racemic β-derivatives and ethyl DL-α-aminobutyrate hydrochloride was collected. Trituration with a small volume of water resulted in the practical removal of the ester hydrochloride. After recrystallization from ethanol, ethyl (*N*-benzyl-β-DL-aspartyl)-α-aminobutyrate, m. p. 183° (0·9 g., 27%), was obtained.[2] The m. p. was raised to 186° by a second recrystallization from ethanol. The ethanolic mother-liquor was evaporated and the residue recrystallized from water, yielding the second racemic modification of the β-dipeptide derivative, m. p. 161° (0·5 g., 15%).[2] To the original filtrate of the mixture (acetone) ether was added until the appearance of cloudiness and the whole was left at 0° for 7 days. Ethyl (*N*-benzyl-α-DL-aspartyl)-DL-α-aminobutyrate which crystallized was recrystallized from water, then having m. p. 85° (1 g., 30%).

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883. NN′-*Dialkyl*-DL-*asparagines*.

By Y. LIWSCHITZ, YOLAN EDLITZ-PFEFFERMANN, and Y. SHORR.

FEW *NN*′-dialkylasparagines, $NHR'\cdot CH(CO_2H)\cdot CH_2\cdot CO\cdot NHR$, have been reported,[1] apart from such dialkyl derivatives in which R′ is benzyl and which served as an intermediate masking group.[2] However, any desired compound of this class may be prepared by condensation of the appropriate alkylmaleamic acid with an amine, the alkyl radical of which becomes the *N*-substituent (R′). Preparation of alkylmaleamic acids [2] is nearly always quantitative and the subsequent addition of amines to the double bond gives satisfactory yields in most cases. Although for steric reasons β-aspartylamides are produced predominantly, formation of α-isomers has been established in all cases so far encountered, except *NN*′-di-*n*-hexyl-DL-asparagine, by a positive biuret reaction.[3] These derivatives of α-asparagine, however, are soluble in the reaction solvent (pyridine), whereas the β-asparagines are precipitated. In a few cases, when the yield of the α-isomers formed seemed appreciable, their isolation was performed.

TABLE 1. *Preparation of* NN′-*dialkyl*-DL-*asparagines*.

R	R′	Yield (%)	M. p.	Reflux time (min.)	Formula	C (%) Found	C (%) Reqd.	H (%) Found	H (%) Reqd.	N (%) Found	N (%) Reqd.
Pr^n	Bu^n	48	228°	75	$C_{11}H_{22}O_3N_2$	58·0	57·4	9·8	9·6	12·1	12·2
	n-Pentyl	55	229	60	$C_{12}H_{24}O_3N_2$	58·8	59·0	9·4	9·9	11·3	11·4
	*iso*Pentyl	54	216	60	$C_{12}H_{24}O_3N_2$	59·1	59·0	9·6	9·9	11·2	11·4
	n-Hexyl	45	226	60	$C_{13}H_{26}O_3N_2$	60·8	60·4	9·8	10·1	10·6	10·9
Bu^n	*n*-Hexyl	68	214—217	75	$C_{14}H_{28}O_3N_2$	61·3	61·7	10·2	10·4	10·1	10·3
n-Hexyl	Pr^n	47	226	65	$C_{13}H_{26}O_3N_2$	60·1	60·4	9·9	10·1	10·8	10·9
	Pr^i	20	192	150	$C_{13}H_{26}O_3N_2$	61·2	60·4	9·9	10·1	10·7	10·9
	Bu^n	51	220	40	$C_{14}H_{28}O_3N_2$	61·6	61·7	10·2	10·4	10·2	10·3
	n-Pentyl	40	221	120	$C_{15}H_{30}O_3N_2$	63·6	62·9	10·8	10·6	9·5	9·8
	*iso*Pentyl	35	212	120	$C_{15}H_{30}O_3N_2$	63·0	62·9	10·1	10·6	9·7	9·8
	*cyclo*Hexyl	24	197	150	$C_{16}H_{30}O_3N_2$	64·5	64·4	10·2	10·1	9·1	9·4

Experimental.—M. p.s were determined in a Fisher–Johns apparatus.

Preparation of NN′-*dialkyl*-DL-*asparagines*. The *N*-alkylmaleamic acid (0·02 mole) and the

[1] McMillan and Albertson, *J. Amer. Chem. Soc.*, 1948, **70**, 3778.
[2] Liwschitz, Edlitz-Pfeffermann, and Lapidoth, *ibid.*, 1956, **78**, 3069.
[3] Liwschitz and Zilkha, *ibid.*, 1954, **76**, 3698.

amine (0·02 mole) were heated in pyridine (20 ml.) under reflux (for reaction times, etc., see Tables 1 and 2), the product being precipitated. This was washed with acetone and generally recrystallized from aqueous ethanol.

TABLE 2. *Preparation of* NN'-*dialkyl*-DL-*asparagines.*

R = R'	Yield (%)	M. p.	Reflux time (min.)	Formula	C (%) Found	C (%) Reqd.	H (%) Found	H (%) Reqd.	N (%) Found	N (%) Reqd.
Pr^n	87	238°	60	$C_{10}H_{20}O_3N_2$	55·6	55·5	9·0	9·3	12·9	12·9
n-Hexyl	84	221	45	$C_{14}H_{28}O_3N_2$	63·8	63·9	10·5	10·7	9·1	9·3
p-C_6H_4·OMe * ...	8	225	60	$C_{15}H_{20}O_5N_2$	61·7	62·6	5·1	5·8	7·9	8·1

* N-p-*Methoxyphenylmaleamic acid*, m. p. 200° (Found: C, 59·0; H, 5·0; N, 6·3. $C_{11}H_{11}O_4N$ requires C, 59·6; H, 5·0; N, 6·3%).

TABLE 3. *Isolation of* NN'-*dialkyl*-DL-α-*asparagines.*

R	R'	Yield (%)	M. p.	Reflux time (min.)	Formula	C (%) Found	C (%) Reqd.	H (%) Found	H (%) Reqd.	N (%) Found	N (%) Reqd.
Pr^n	*n*-Hexyl	34	108°	60	$C_{12}H_{24}O_3N_2$	60·0	60·4	9·9	10·1	10·3	10·9
Bu^n	*n*-Hexyl	14	103	75	$C_{14}H_{28}O_3N_2$	61·8	61·7	10·4	10·4	10·2	10·3
n-Hexyl	*iso*Pentyl	16	142	120	$C_{15}H_{30}O_3N_2$	62·2	62·9	10·5	10·6	9·0	9·8

Isolation of NN'-*dialkyl*-DL-α-*asparagines.* The pyridine mother-liquor was evaporated and the residue triturated with acetone. Recrystallization from ethyl acetate resulted in complete separation from small amounts of β-isomer, since the latter, being insoluble in that solvent, could be eliminated by filtration. Results are summarized in Table 3.

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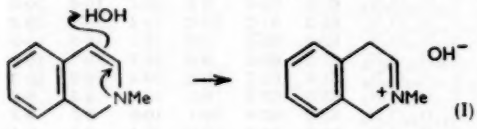
884. *Reduction of Quaternized* iso*Quinoline Derivatives with Sodium Borohydride.*

By R. MIRZA.

*iso*QUINOLINE METHIODIDE is reduced by sodium borohydride in aqueous methanol almost quantitatively to 1 : 2 : 3 : 4-tetrahydro-2-methyl*iso*quinoline (Torossian [1] reports an 85% yield by use of potassium borohydride). Similarly, berberine, which can be regarded as a quaternized *iso*quinoline derivative, is reduced to its tetrahydro-derivative, (±)-canadine, and the methiodide of papaverine gave (±)-laudanosine, both in excellent yields.* However, reduction in dry methanol gave only tars.

A possible mechanism involves preliminary reduction of the metho-salt to 1 : 2-dihydro-2-methyl*iso*quinoline,[3, 4] which in presence of water could be converted into 1 : 4-dihydro*iso*quinolinium hydroxide (I); the latter should be easily reducible to the tetrahydro*iso*quinoline. In absence of water, it is not possible for the 1 : 2-dihydro-2-methyl derivative to go through the process indicated and in view of the labile nature of the 1 : 2-dihydro*iso*quinolines a tarry product is not surprising.



(I)

* Our work was independent of that of Witkop.[2]

[1] Torossian, *Compt. rend.*, 1952, **235**, 1312.
[2] Witkop, *J. Amer. Chem. Soc.*, 1953, **75**, 4474.
[3] Whaley and Robinson, *J. Amer. Chem. Soc.*, 1953, **75**, 2008.
[4] Panouse, *Compt. rend.*, 1951, **233**, 260.

It is known [5] that lithium aluminium hydride reduces *iso*quinoline methiodide to 1 : 2-dihydro-2-methyl*iso*quinoline, berberine to dihydroberberine, and papaverine methiodide to 1 : 2-dihydro-*N*-methylpapaverine. These results are easily understood in view of the mechanism of reduction now proposed. Reductions by lithium aluminium hydride occur in complete absence of water and thus the carbon–carbon double bond in the 1 : 2-dihydro-compound is not thus reducible. Dihydroberberine is readily reduced to (±)-canadine in aqueous methanol by sodium borohydride.

It has been reported that borohydride reduces pyridine methiodide to 1 : 2 : 3 : 6-tetrahydro-1-methylpyridine,[4] methyl nicotinate methiodide to arecoline,[6] methylsempervirine chloride to hexahydromethylsempervirine,[7] and harman methobromide to tetrahydro-*Py*-*N*-methylharman.[8] These compounds have a close relationship to *iso*quinoline salts and a similar mechanism explains their reduction. The necessity for the presence of water has previously not been realised, and may apply in these cases.

Experimental.—Reduction of iso*quinoline methiodide.* Sodium borohydride (500 mg.) and *iso*quinoline methiodide (540 mg.) in methanol (10 ml.) and water (1 ml.) were refluxed for 10 min. After addition of more water (50 ml.) the mixture was extracted with chloroform. Evaporation of chloroform gave a liquid residue which in methanol (10 ml.) gave 1 : 2 : 3 : 4-tetrahydro-2-methyl*iso*quinoline picrate (720 mg.), m. p. and mixed m. p. 147—148°.

Other reductions. Berberine hydrochloride (1·0 g.) on reduction gave (±)-canadine (720 mg.), m. p. 177—178°; papaverine methiodide (1·0 g.; anhyd.) gave (±)-laudanosine (690 mg.), m. p. 113—114°; dihydroberberine (50 mg.) gave (±)-canadine (20 mg.). In all these reductions an equal weight of sodium borohydride was used. The products were purified by sublimation and their identities established by mixed m. p.

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[*Received, May 30th,* 1957.]

[5] Karrer and Schmid, *Helv. Chim. Acta*, 1949, **32**, 960.
[6] Panouse, *Compt. rend.*, 1951, **233**, 1200.
[7] Witkop, *J. Amer. Chem. Soc.*, 1953, **75**, 3361.
[8] Gray, Spinner, and Cavallito, *ibid.*, 1954, **76**, 2793.

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885. *The Chemistry of Gum Labdanum. Part III.* A Proof of the β-Configuration of the $C_{(9)}$ Side-chain of Labdanolic Acid.*

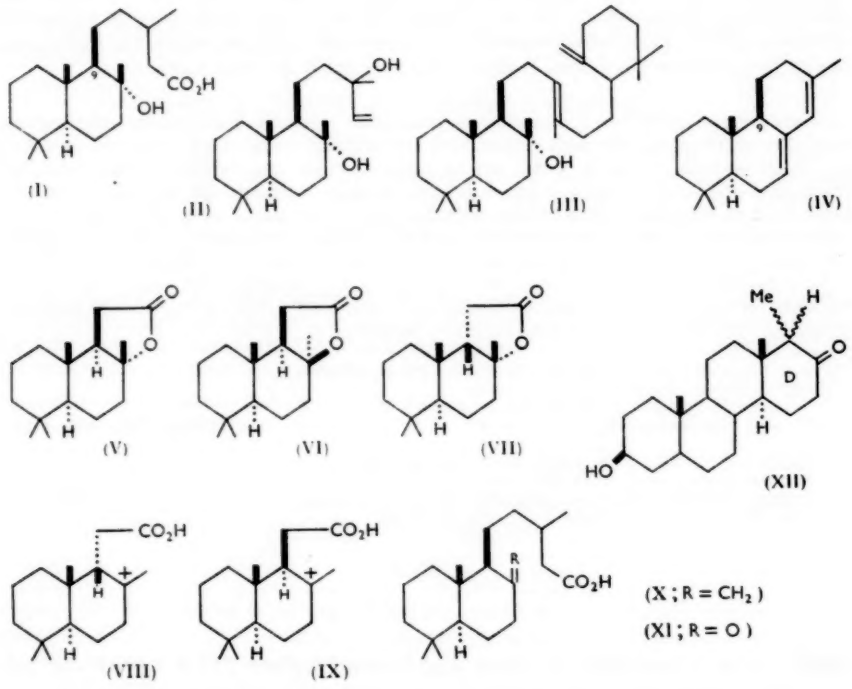
By J. D. Cocker and T. G. Halsall.

The structure of labdanolic acid has already been shown to be (I), it being assumed that the $C_{(9)}$ side-chain of sclareol (II) and ambrein (III), with which labdanolic acid has been related, has the β-configuration.[1] Although there is strong circumstantial evidence in favour of this configuration it has not yet been proved. Rotational evidence [2-4] concerning certain degradation products of sclareol (and manoöl) (*e.g.*, IV) shows that these have the carbon chain β at $C_{(9)}$. If it is assumed that inversion does not occur during the preparation of the degradation products then the $C_{(9)}$ side-chain of sclareol must have the β-configuration. Klyne [4] has also pointed out that the isomerisation with ethanolic

* Part II, *J.*, 1956, 4262.

[1] Cocker and Halsall, *J.*, 1956, 4262.
[2] Ruzicka, Zwicky, and Jeger, *Helv. Chim. Acta*, 1948, **31**, 2143.
[3] Barton, *Quart. Rev.*, 1949, **3**, 61.
[4] Klyne, *J.*, 1953, 3072.

hydrogen bromide of the lactone (V), obtained by oxidation from sclareol [5,6] and ambrein,[7] to a second lactone (VI) is most satisfactorily explained by assuming that the isomerisation involves the rearrangement of a *trans*-fused lactone system (cf. V) to a *cis*-fused system (cf. VI). It is conceivable, however, that the lactone (VI) could arise from the *cis*-lactone (VII) which would correspond to the side-chain of sclareol having the α-configuration. The mechanism of such a change could involve O–alkyl fission of the lactone (VII) under acidic conditions,[cf. 8] giving the ion (VIII). This could then rearrange by loss and addition of a proton at $C_{(9)}$ to the ion (IX) which would cyclise to the lactone (VI). This type of



isomerisation of lactones through an unsaturated intermediate has been suggested to explain some of the rearrangements of the desmotroposantonins.[9,10]

Evidence has now been obtained that the side-chain of labdanolic acid, and hence of sclareol and ambrein, has the stable β-configuration. Labd-8(20)-en-15-oic acid (X) was ozonised in ethyl acetate at −70° and the ozonide decomposed with zinc dust and acetic acid at 10° to the keto-acid (XI). These conditions are regarded as sufficiently mild to preclude epimerisation at $C_{(9)}$ as Jones, Lewis, Shoppee, and Summers [11] were able to prepare coprostan-6-one by oxidation of the corresponding alcohol in acetic acid at room

[5] Ruzicka and Janot, *Helv. Chim. Acta*, 1931, **14**, 645.
[6] Ruzicka, Seidel, and Engel, *ibid.*, 1942, **25**, 621.
[7] Lederer and Mercier, *Experientia*, 1947, **3**, 188.
[8] Stimson, *J.*, 1955, 2673.
[9] Huang-Minlon, *J. Amer. Chem. Soc.*, 1948, **70**, 611.
[10] Barton, *J. Org. Chem.*, 1950, **15**, 466.
[11] Jones, Lewis, Shoppee, and Summers, *J.*, 1955, 2876.

temperature for 18 hr. Coprostan-6-one is very labile, being converted into cholestan-6-one by acid and alkali. After treatment with alkali the keto-acid (XI) was unchanged. If the side-chain had had the α-configuration epimerisation would have been expected corresponding to the change from an axial to an equatorial conformation. Ramirez and Stafiej have shown that in the presence of alkali the analogous epimeric 17*a*-methyl-17-oxo-D-homosteroid (XII), with the $C_{(17a)}$ methyl group α-orientated, equilibrates to a mixture in which the 17*a*-β-methyl epimer predominates.

Experimental.—M. p.s were determined on a Kofler block and are corrected.

Ozonolysis of labd-8(20)-en-15-oic acid (X). The acid (5·03 g.) in ethyl acetate (200 c.c.) was treated with ozonised oxygen at −70° until a faint blue colour persisted. The excess of ozone was removed by passing a stream of nitrogen through the solution for 10 min. The mixture was then stirred at 10° with acetic acid (80 c.c.) and zinc dust (30 g.) until it no longer coloured starch–iodide paper. The zinc dust was removed and washed with ethyl acetate. Ether (100 c.c.) was added to the filtrate and washings. The solution was then washed with water, dried, and evaporated to give a gum which afforded 20-nor-8-oxolabdan-15-oic acid as needles (from methanol–water), m. p. 110°, identical with the product (m. p. 110·5—111°; $[\alpha]_D$ −40°) [12] obtained by hydrolysis of methyl 20-nor-8-oxolabdan-15-oate.

Attempted isomerisation of 20-nor-8-oxolabdan-15-oic acid. The acid (0·24 g.) was heated under reflux for 1 hr. with methanolic potassium hydroxide (20%; 10 c.c.). After being kept at 20° for 1 hr. the mixture was poured into water, and dilute hydrochloric acid was added. Ethereal extraction of the solution afforded needles (from methanol–water), m. p. 109—111°, which were identified as starting material by m. p., mixed m. p., and rotation.

One of the authors (J. D. C.) thanks the Department of Scientific and Industrial Research for a maintenance grant.

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[12] Ramirez and Stafiej, *J. Amer. Chem. Soc.*, 1955, **77**, 134; *Chem. and Ind.*, 1955, 1180.

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886. *Some 4-Alkylaminoquinolines.*

By ALFRED CAMPBELL and (MRS.) S. D. CAVALLA.

IT having been found that 4-heptylamino-6-methoxyquinaldine had considerable antitubercular activity *in vitro*, a series of related aminoquinolines was prepared. As can be seen from the Table, peak activity was found in 7-chloro-4-heptylaminoquinoline (No. 9) but tests *in vivo* in mice were negative.

Experimental.—With the exception of compounds 1 and 7, a modification of Holcomb and Hamilton's method [1] was used in the preparation of these materials, *viz.*:

The substituted 4-chloroquinoline (0·1 mole) and the base (0·2 mole) were refluxed for 4 hr. (No. 2 required 17 hr. at 140°). The warm viscous mixture was dissolved in methanol (25 ml.) and poured into an excess of 2N-sodium hydroxide, and the precipitate extracted with ether (2 × 200 ml.). After being dried (K_2CO_3), the ether was removed and the base (Nos. 3, 4, 9) crystallised from acetone. Low-melting bases (Nos. 2, 5, 6, 8) were converted into the hydrochlorides which were crystallised from absolute methanol–ether.

4-Heptylaminoquinoline. A solution of 7-chloro-4-heptylaminoquinoline (10 g.) in ethanol (250 ml.) containing N-sodium hydroxide (38 ml.) was shaken with palladised charcoal in hydrogen (924 ml. of hydrogen were absorbed). The filtered solution was concentrated under

[1] Holcomb and Hamilton, *J. Amer. Chem. Soc.*, 1942, **64**, 1309.

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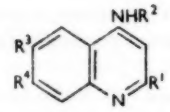
reduced pressure and the product crystallised once from ethanol; pure **4-*heptylaminoquinoline*** (7·5 g.; 82%) formed rhombohedra, m. p. 107—108°.

4-*Amino*-6-*methoxyquinaldine*. Phenylhydrazine (5·4 g.), 4-chloro-6-methoxyquinaldine (10·4 g.), and medicinal paraffin (50 ml.) were heated at 200° for 1 hr. The yellow solid was collected and rinsed with ether before being suspended in concentrated hydrochloric acid (100 ml.). Zinc dust was then added gradually to the boiling suspension until the yellow solid had completely dissolved. The cooled solution was made alkaline with 28% aqueous ammonia and the product extracted with ethyl acetate. Crystallisation from benzene or acetone gave **4-*amino*-6-*methoxyquinaldine*** (2·5 g.; 26%) as needles, m. p. 207—208°.



No.	R^1	R^2	R^3	R^4	M. p.	Activity *
1	CH_3	H	OCH_3	H	207—208°	20
2	CH_3	n-C_6H_5	OCH_3	H	217—218	20
3	CH_3	n-C_6H_{13}	OCH_3	H	134—135	2·5
4	CH_3	n-C_7H_{15}	OCH_3	H	132—133	1·25
5	CH_3	n-$C_{10}H_{21}$	OCH_3	H	158—160	4
6	CH_3	n-$C_{16}H_{33}$	OCH_3	H	159—161	5
7	H	n-C_7H_{15}	H	H	107—108	5
8	H	n-C_7H_{15}	OCH_3	H	208—210 (decomp.)	20
9	H	n-C_7H_{15}	H	Cl	114—115	0·62

	Found, %				Required, %		
No.	C	H	N	Formulæ	C	H	N
1	70·0	6·5	15·0	$C_{11}H_{12}ON_2$	70·2	6·4	14·9
2	60·0	7·7	9·2	$C_{15}H_{20}ON_2,HCl,H_2O$	60·2	7·8	9·3
3	75·1	9·0	10·4	$C_{17}H_{24}ON_2$	75·0	8·9	10·3
4	75·3	8·9	9·7	$C_{18}H_{26}ON_2$	75·5	9·1	9·8
5	68·7	9·2	7·8	$C_{21}H_{31}ON_2,HCl$	69·1	9·1	7·7
6	72·0	10·2	6·2	$C_{27}H_{44}ON_2$	72·2	10·1	6·2
7	79·1	9·2	11·6	$C_{16}H_{22}N_2$	79·3	9·2	11·6
8	66·0	8·2	9·2	$C_{17}H_{24}ON_2,HCl$	66·1	8·2	9·1
9	69·3	7·6	9·9	$C_{16}H_{21}N_2Cl$	69·4	7·7	10·1

* In μg./ml.; causing complete inhibition of growth in *M. tuberculosis* H37Rv. Compounds No. 1, 3, 4, and 9 crystallised as needles from acetone; compound No. 7 formed rhombohedra from ethyl alcohol; and compounds No. 2, 5, 6, and 8 needles from methyl alcohol–ether.

PARKE, DAVIS & COMPANY, LIMITED, HOUNSLOW, MIDDLESEX. [*Received, June 5th*, 1957.]

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887. *Ultraviolet Absorption Spectra and Paper Chromatography of 2-Thiohydantoins.*

By D. T. ELMORE and J. R. OGLE.

SINCE several methods of stepwise degradation of peptides involve the liberation and identification of either the *C*- or the *N*-terminal amino-acid as the corresponding 2-thiohydantoin,[1-4] we investigated methods for the recognition and quantitative determination of these compounds by chromatography and absorption spectrophotometry, and have extended the range of earlier chromatographic studies [1,3] to include a number of compounds described recently.[5] Of the solvents already described for the paper chromatography of

[1] Edward and Nielson, *Chem. and Ind.*, 1953, 197.
[2] Kenner, Khorana, and Stedman, *J.*, 1953, 673.
[3] Dautrevaux and Biserte, *Compt. rend.*, 1955, **240**, 1153.
[4] Elmore and Toseland, *J.*, 1954, 4533.
[5] Elmore, Ogle, and Toseland, *J.*, 1956, 192.

2-thiohydantoins, butan-1-ol saturated with water [1] was satisfactory (Table 1), but propionic acid–light petroleum (b. p. 100—120°) [2] did not give discrete spots. The system of Dautrevaux and Biserte [3] as well as a new solvent (C, Table 1) occasionally gave rise to multiple spots. The reason for this is not certain, but we believe that with solvent C,

TABLE 1.

No.	Compound	R_F values with standard deviation in parentheses: Sol. A	Sol. B	Sol. C [a]
1	2-Thiohydantoin	0·45 (0·04)	0·14 (0·02)	0·08 (0·02)
2	5-Methyl-2-thiohydantoin	0·64 (0·03)	0·33 (0·05)	0·22 (0·05)
3	5-Ethyl-2-thiohydantoin	0·72 (0·03)	0·53 (0·05)	0·42 (0·07)
4	5-*n*-Propyl-2-thiohydantoin	0·78 (0·03)	0·67 (0·06)	0·72 (0·05)
5	5-*iso*Propyl-2-thiohydantoin	0·78 (0·03)	0·68 (0·05)	0·69 (0·04)
6	5-*n*-Butyl-2-thiohydantoin	0·81 (0·04)	0·84 (0·05)	0·98 (0·02)
7	5-*iso*Butyl-2-thiohydantoin	0·82 (0·03)	0·84 (0·05)	1·00
8	5-*sec.*-Butyl-2-thiohydantoin	0·81 (0·03)	0·82 (0·04)	0·99 (0·02)
9	1-Methyl-2-thiohydantoin	0·59 (0·04)	0·31 (0·05)	0·25 (0·04)
10	5-Benzyl-2-thiohydantoin	0·77 (0·04)	0·65 (0·05)	0·55 (0·04)
11	5-*p*-Hydroxybenzyl-2-thiohydantoin	0·72 (0·03)	0·21 (0·04)	0·06 (0·02)
12	5-3′-Indolylmethyl-2-thiohydantoin	0·83 (0·03)	0·76 (0·06)	0·62 (0·04)
13	Pyrrolidino(1′ : 2′-1 : 5)-2-thiohydantoin	0·71 (0·04)	0·50 (0·04)	0·52 (0·04)
14	5-Methylthiomethyl-2-thiohydantoin	0·71 (0·03)	0·40 (0·05)	0·29 (0·07)
15	5-2′-Methylthioethyl-2-thiohydantoin	0·75 (0·04)	0·56 (0·05)	0·42 (0·05)
16	5-2′-Methylsulphonylethyl-2-thiohydantoin	0·48 (0·06) [b]	streaks	0·00
17	5-Carboxymethyl-2-thiohydantoin	0·12 (0·03)	0·10 (0·02)	0·03 (0·01)
18	5-2′-Carboxyethyl-2-thiohydantoin	0·28 (0·05)	0·17 (0·05)	0·05 (0·00)
19	5-Carbamoylmethyl-2-thiohydantoin	0·27 (0·04)	0·07 (0·03)	0·03 (0·00)
20	5-2′-Carbamoylethyl-2-thiohydantoin	0·33 (0·04)	0·10 (0·01)	0·03 (0·00)
21	5-Sulphomethyl-2-thiohydantoin	0·06 (0·02)	0·00	0·00
22	5-3′-Aminopropyl-2-thiohydantoin,HCl,$\frac{1}{2}$H$_2$O	0·12 (0·03)	0·02 (0·00)	0·00
23	5-4′-Aminobutyl-2-thiohydantoin,HCl	0·12 (0·02)	0·03 (0·00)	0·00
24	5-3′-Guanidinopropyl-2-thiohydantoin,HCl	0·20 (0·04)	0·02 (0·00)	0·00
25	5-4′-Glyoxalinylmethyl-2-thiohydantoin,HCl	streaks	0·02 (0·00)	0·00

[a] The figures in this column refer to the ratio (distance travelled by compound)/(distance travelled by No. 7). [b] Elongated spot.

multiple spots may arise from photochemical decomposition (see below) during equilibration in the light, since chromatograms equilibrated and run in the dark were satisfactory. This modification did not improve the results with the other system.[3] Useful separation of basic and acidic 2-thiohydantoins was obtained on paper electropherograms.

Ultraviolet absorption data for 2-thiohydantoins are recorded in Table 2. The majority of compounds have maximal absorption at 266 ± 1 mμ (ε 18,500 ± 700). An aliphatic group at $C_{(5)}$ has bathochromic and hyperchromic effects as revealed by a comparison of the spectra of 5-alkyl-2-thiohydantoins with that of 2-thiohydantoin. Simultaneous substitution of $N_{(1)}$ and $C_{(5)}$ in pyrrolidino(1′ : 2′-1 : 5)-2-thiohydantoin causes a greater bathochromic effect ($\lambda_{max.}$ 271 mμ), although $\varepsilon_{max.}$ is considerably lower than normal. The latter effect may result from substitution at $N_{(1)}$, since 1-methyl-2-thiohydantoin has an abnormally low extinction coefficient. Absorption spectra of 2-thiohydantoins derived from lysine, ornithine, and arginine are characteristic since both $\lambda_{max.}$ and $\varepsilon_{max.}$ are lower than normal. The absorbance ratio, $A_{270\ m\mu}/A_{260\ m\mu}$, appears to be a useful constant for the characterisation of 2-thiohydantoins; for example, 5-alkyl-2-thiohydantoins have an absorbance ratio of 1·01—1·05, but chain-branching or the introduction of an aryl or a heterocyclic group at $C_{(1')}$ increases this significantly. A higher absorbance ratio also results from the presence of a sulphur atom in the side-chain at $C_{(5)}$.

Solutions of 2-thiohydantoins were rather unstable in light and the characteristic absorption bands disappeared when a solution was kept on the bench for a few days. The mechanism of the photochemical decomposition of 2-thiohydantoins is unknown,

but after irradiation of a solution of 5-*iso*propyl-2-thiohydantoin by a high-pressure mercury arc for 6 days, ammonium sulphate (25% yield) was the only identifiable product.

Improved methods for the preparation of some 2-thiohydantoins are recorded in the Experimental section.

TABLE 2.

No.	$\lambda_{max.}$ (mμ)	$\lambda_{min.}$ (mμ)	$\lambda_{max.}$ (mμ)	$\varepsilon_{266} \pm 95\%$ confidence limits	Absorbance ratio [a]
1	263—264	237	222	17,030 ± 270	0·87
2	265—266	238—239	224	18,210 ± 440	1·01
3	266	238—239	224—225	17,760 ± 330	1·03
4	265—266	239	225	18,220 ± 430	1·04
5	266—267	239	225	18,100 ± 350	1·10
6	266	238—239	224—225	18,670 ± 460	1·05
7	266	238—239	224	18,970 ± 390	1·04
8	266	239	225	18,710 ± 300	1·08
9	265—266	243—244	230	15,280 [b]	1·02
10	267	240	223—225 [c]	17,820 ± 420	1·16
11	268	240	225	17,900 ± 120	1·19
12	278	247	219	13,000 ± 390	1·76
13	271	248	233—234	14,260 [b]	1·44
14	267	238	223—224	[d]	1·12
15	267	239	225	19,260 ± 490	1·16
16	267	239	225	18,510 ± 430	1·12
17	266	239	224	19,210 ± 240	1·02
18	266	238	225	18,810 ± 350	1·07
19	265—266	238—239	224	19,010 ± 410	1·02
20	266	239	225	18,370 ± 320	1·08
21	262—263	238—239	225	[e]	0·76
22	262—263	238	225	15,100 ± 260	0·79 [f]
23	262	238	224	15,570 ± 300	0·77
24	261—262	238	225	16,470 [f]	0·77 [f]
25	267	239	—	18,170 ± 480	1·15

[a] $A_{270\ m\mu}/A_{266\ m\mu}$.
[b] The value of ε is a mean of two determinations. [c] Point of inflexion. [d] Insufficient material for more than one determination. [e] Too hygroscopic for determination of ε. [f] Aqueous solutions used for spectral determinations.

ε ± 95% confidence limits at other wavelengths: No. 12, 18,080 ± 450 at 278 mμ; No. 13, 15,640 at 271 mμ; No. 22, 16,180 ± 30 at 262 mμ; No. 23, 16,580 ± 310 at 262 mμ; No. 24, 17,520 at 261 mμ.

Experimental.—The following systems were used for paper chromatography of 2-thiohydantoins: (A) butan-1-ol saturated with water on Whatman No. 11 paper, (B) *cyclo*hexane–butan-1-ol–90% acetic acid (60 : 20 : 20) on Whatman No. 52 paper, and (C) *cyclo*hexane–propan-2-ol–90% acetic acid (65 : 15 : 20) on Whatman No. 52 paper in the dark. System B was run on ascending chromatograms in a constant-temperature room at 25° after equilibration for several hours. Both phases of system C were used for equilibration and chromatograms were irrigated with the upper phase for about 24 hr. (The lower end of the paper was serrated with pinking shears.)

Electrophoresis for 14 hr. on Whatman No. 54 paper (4v/cm.) in a buffer (pH 5·9) consisting of 0·025M-citric acid and 0·05M-disodium hydrogen phosphate (2 : 3) caused the following migrations: compounds (17) and (21), 12 cm. to anode; (18), 9·5 cm. to anode; (22) and (23), 17 cm. to cathode; (24), 15 cm. to cathode; (25), 14 cm. to cathode.

All spectra, except where otherwise indicated in Table 2, were measured on freshly-prepared solutions in 95% ethanol, a Beckman DU ultraviolet absorption spectrophotometer being used. Matched quartz cells (Thermal Syndicate Ltd., Wallsend, Northumberland) with optical path 1 ± <0·001 cm. were employed. The absorbance was determined at several dilutions, and all compounds obeyed Beer's law over the range 1·5—5·0 × 10^{-5} molar. The molar extinction coefficient was calculated from the slope of the graph of absorbance against concentration by the least-squares method. Replicate determinations of ε by this method were tested for compatibility by the *t* test, following standard statistical methods, and sufficient measurements were obtained to give a mean value of ε with 95% confidence limits of <±500.

1-Methyl-2-thiohydantoin. *N*-Benzoylthiocarbamoylsarcosine ethyl ester[5] (1 g.) was heated under reflux in ethanol (50 c.c.) and 3N-hydrochloric acid (50 c.c.) for 3 hr. After removal of solvents under reduced pressure, the residue was partitioned between ethyl acetate and saturated sodium hydrogen carbonate, and the upper layer was washed and dried. Addition of light petroleum (b. p. 60—80°) afforded the product (0·21 g.), m. p. 224—226° (decomp.) after recrystallisation from 95% ethanol.

5′-Oxopyrrolidino(1′ : 2′-1 : 5)-*2-thiohydantoin.* DL-5-Oxopyrrolidine-2-carboxylic acid (2 g.) and dry ammonium thiocyanate (1·5 g.) were heated for 20 min. at 100° in acetic anhydride (9 c.c.) and glacial acetic acid (1 c.c.). Water (25 c.c.) was added; the product (1·0 g.), m. p. 204—205°, crystallised overnight in the refrigerator.

5-2′-Carboxyethyl-2-thiohydantoin. A solution of 5′-oxopyrrolidino(1′ : 2′-1 : 5)-2-thiohydantoin (0·78 g.) in 4N-hydrochloric acid (25 c.c.) was evaporated to dryness on the steam-bath. The residual gum crystallised on cooling; the product (0·60 g.) had m. p. 121—122° after recrystallisation from water.

5-4′-Aminobutyl-2-thiohydantoin hydrochloride. The oil, which resulted from the reaction of ε-*N*-benzyloxycarbonyl-L-lysine (5 g.) with ammonium thiocyanate in acetic anhydride–acetic acid,[5] was shaken with a solution (50% w/v; 30 c.c.) of hydrogen bromide in acetic acid for 30 min. The gum, which resulted from pouring the mixture into ether (600 c.c.), was converted into the thiohydantoin (0·55 g.), m. p. 236—237° (decomp.), by hot 3N-hydrochloric acid as described previously.[5]

The authors thank Mr. H. J. V. Tyrrell for valuable discussions, Mrs. W. Fletcher for technical assistance, and Imperial Chemical Industries Limited for financial support.

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888. *The Reaction of Benzaldehyde with Ammonium Acetate.*

By S. TRIPPETT.

PINNER[1] in 1889 reported that benzaldehyde, when refluxed with twice its weight of ammonium acetate, gave a compound, m. p. 247°, to which he assigned the formula $C_{42}H_{37}O_2N_3$. It was sparingly soluble in the usual organic solvents and dissolved unchanged in concentrated sulphuric acid. The reaction has now been reinvestigated.

When benzaldehyde is refluxed with ammonium acetate or ammonium propionate for 3—4 hr. a highly crystalline neutral compound, $C_{28}H_{24}ON_2$, m. p. 259°, is obtained in 60% yield. It shows infrared absorption at 3·05(w), 6·09(s), and 6·5 μ(s), suggesting the presence of a secondary amide group, and brief treatment with 70% sulphuric acid gives benzaldehyde and a base, $C_{21}H_{20}ON_2$, which from its infrared spectrum is also a secondary amide. Further hydrolysis of this with 70% sulphuric acid gives benzoic acid and *meso*-1 : 2-diphenylethylenediamine. The base is therefore *N*-benzoyl*meso*-1 : 2-diphenylethylenediamine and the original compound *N*-benzoyl-*N*′-benzylidene*meso*-1 : 2-diphenylethylenediamine.

The formation of a 1 : 2-diphenylethylenediamine derivative under such mild conditions probably involves a benzoin-type condensation. This view is supported by the effect of substituents on the course of the reaction. Products analogous to that from benzaldehyde are formed rapidly from *p*-chloro- and *m*-nitro-benzaldehyde but under the same conditions *p*-tolualdehyde and anisaldehyde give no comparable compounds. *p*-Nitrobenzaldehyde reacts rapidly but not as expected.

Experimental.—Reaction of benzaldehyde with ammonium acetate. Benzaldehyde (30 g.) was refluxed with ammonium acetate (60 g.) for 3 hr., the mixture cooled and the product filtered

[1] Pinner, *Ber.*, 1889, **22**, 1598.

and washed repeatedly with ethanol. Recrystallisation from butan-1-ol gave N-*benzoyl*-N'-*benzylidene*meso-1 : 2-*diphenylethylenediamine* (60%), m. p. 258—259° (Found: C, 83·1; H, 5·95; N, 7·05. $C_{28}H_{24}ON_2$ requires C, 83·1; H, 5·9; N, 6·9%).

The above product (5 g.) was refluxed with 70% sulphuric acid (60 ml.) for 20 min. and the solution poured on ice. The resulting suspension was extracted with ether and then made alkaline with 2N-sodium hydroxide. Filtration of the precipitate and crystallisation from aqueous ethanol gave N-*benzoyl*meso-1 : 2-*diphenylethylenediamine*, m. p. 204—205° (Found: C, 79·5; H, 6·25; N, 8·95. $C_{21}H_{20}ON_2$ requires C, 79·65; H, 6·3; N, 8·85%). The *picrate* (from alcohol) had m. p. 204° (decomp.) (Found: N, 12·6. $C_{27}H_{23}O_8N_5$ requires N, 12·85%). Refluxing with acetic anhydride for 0·5 hr. gave the acetate, m. p. (from nitrobenzene) 316° (lit.[2] m. p. 316°) (Found: C, 77·1; H, 6·2; N, 7·9. Calc. for $C_{23}H_{22}O_2N_2$: C, 77·1; H, 6·2; N, 7·8%).

Hydrolysis of the original benzylidene-benzoate or further hydrolysis of the benzoate with 70% sulphuric acid under reflux for 1 hr. gave as the basic product of hydrolysis *meso*-1 : 2-diphenylethylenediamine, m. p. (from ether at 0°) 120·5—121·5° (Found: C, 79·5; H, 7·5; N, 13·5. Calc. for $C_{14}H_{16}N_2$: C, 79·25; H, 7·6; N, 13·2%).

meso-1 : 2-*Di*-p-*chlorophenylethylenediamine*. *p*-Chlorobenzaldehyde (10 g.) was refluxed with ammonium acetate (20 g.) for 3 hr. and the product crystallised from butan-1-ol to give N-p-*chlorobenzoyl*-N'-p-*chlorobenzylidene*meso-1 : 2-*di*-p-*chlorophenylethylenediamine* (65%), m. p. 249° (Found: C, 62·0; H, 3·7; N, 5·15. $C_{28}H_{20}ON_2Cl_4$ requires C, 62·0; H, 3·7; N, 5·2%). Hydrolysis of this with 70% sulphuric acid under reflux for 1 hr. gave meso-1 : 2-*di*-p-*chlorophenylethylenediamine*, m. p. (from ether) 137—138° (Found: C, 60·0; H, 5·0; N, 9·5. $C_{14}H_{14}N_2Cl_4$ requires C, 59·8; H, 5·0; N, 9·95%). Refluxing with acetic anhydride–acetic acid gave the *diacetate*, m. p. (from acetic acid) 360° (Found: C, 59·4; H, 5·0. $C_{18}H_{18}O_2N_2Cl_2$ requires C, 59·15; H, 5·0%).

meso-1 : 2-*Di*-m-*nitrophenylethylenediamine*. *m*-Nitrobenzaldehyde (10 g.) was refluxed with ammonium acetate (20 g.) for 3 hr. The product (7·5 g.) was very insoluble in the usual solvents and could not be recrystallised. Hydrolysis with 70% sulphuric acid under reflux for 1 hr. gave meso-1 : 2-*di*-m-*nitrophenylethylenediamine*, m. p. (from butan-1-ol) 189—190° (Found: C, 55·9; H, 4·9; N, 18·5. $C_{14}H_{14}O_4N_4$ requires C, 55·6; H, 4·7; N, 18·5%). Refluxing with acetic anhydride–acetic acid gave the *diacetate*, m. p. (from acetic acid) 354—355° (Found: C, 56·2; H, 4·8; N, 15·0. $C_{18}H_{18}O_6N_4$ requires C, 56·0; H, 4·7; N, 14·5%).

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[2] Japp and Moir, *J.*, 1900, **77**, 611.